CHEMICAL AND STRONTIUM ISOTOPIC EVOLUTION OF SEDIMENTARY CARBONATE ROCKS IN GEOLOGIC HISTORY

by

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STATEMENT

This thesis is based upon experimental work carried out in the Department of Geophysics and Geochemistry of the Australian National University between May, 1969 and September, 1971. Two field trips to South and central Australia and Tasmania were made in July, 1968 and February, 1970.

The collection of samples have been performed by the author or scientists acknowledged in Appendix 2. All analytical determinations have been carried out by the author.

Apart from those instances where acknowledgement is made, all results and interpretations are solely my responsibility.

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Chapter 1

INTRODUCTION

The general increase of Sr^{87}/Sr^{86} with time has been postulated already by Wickman (1948). This increase should be monitored by sea water, which might serve as an accumulatory system for average Sr^{87}/Sr^{86} derived by weathering of the continental crust. The prediction of Wickman, based on poorly known estimates of Rb and Sr in the crust, was not confirmed by later testing of his hypothesis (Gast, 1955, Ewald et al., 1956 and Gerling and Shukolyukov, 1957). Although these authors observed a slight increase in Sr^{87}/Sr^{86} with decreasing age, the scatter of data was higher than the precision and accuracy of the Sr isotopic measurements at that time. With technical improvements, the increase of Sr^{87}/Sr^{86} of about 1% since Archean, was confirmed by Hedge and Walthall (1963) and Hurley et al. (1965). However, it was believed, that this increase was more or less linear with time. Peterman et al. (1970) published an excellent study of Sr isotopic variations in sea water during Phanerozoic history. They documented quite clearly, that Sr isotopic ratio of sea water was fluctuating with time. It was the original aim of this thesis to test their results and also to obtain data for Paleozoic, which was not well documented, and Precambrian.

The obvious choice for this type of study is sedimentary carbonate rocks, because they are predominantly sea water precipitates, their Rb/Sr ratio is very low and they are also known throughout the whole history of the development of the crust.

Additional major element analyses of selected samples were expected to clarify the problems created by diagenesis and other phenomena. As the project progressed, it became evident, that the composition of rocks during geological history has changed, and that the changes were an indication of

the evolution of the crust, hydrosphere and atmosphere. The results corroborated earlier data published for the Russian Platform and the North America by the Vernardski Institute of Geochemistry in Moscow (Ronov, Vinogradov, Migdisov, Yaroshevski and others acknowledged in the text) and to lesser extent by American authors (Engel, 1963; Daly, 1909 and others). The trends for Australia are much more pronounced than those observed for the Russian Platform and the North America. This might be attributed to better preservation and smaller alteration of Precambrian sequences in Australia. Thus the Sr isotopic data are only a part of the present thesis.

The data and their interpretations are not conclusive and I fully realise that the trends discussed in the present thesis might have been caused by several factors. Nevertheless, the selected interpretations for various elements and trends form an overall coherent picture, and this might support the validity of the given interpretations.

To interprete the accumulated data, it was found necessary to extend the scope of this thesis beyond the field of work undertaken by the Department of Geophysics and Geochemistry. As a result there was a certain loss of guidance and it is quite possible that the interpretations in some cases might be too "enthusiastic", although I hope this is not the case.

Chapter 2 gives descriptions of sequences from which the samples were collected. The detail description of samples is given in Appendix 2. For samples, for which thin-sections were available, Folk's (1959, 1962) classification was used.

Based on these descriptions I attempted to evaluate the type of sedimentary environment and the nature of the contemporaneous climate. The agreement between palaeoclimatic interpretations and palaeomagnetic data supports the validity of the interpretation.

Chapter 3 deals with evolution of sedimentary carbonate rocks in geological history. In general one may observe spreading of sedimentary environments from semi-barred basins in Precambrian into neritic and pelagic environments during Phanerozoic. This is accompanied by simultaneous evolution from ferrugineous dolomites into dolomites and finally into limestones.

Chapter 4 describes analytical methods and their precision and accuracy.

Chapters 5 and 6 deal with the distribution and average concentrations of elements in various types of sedimentary carbonate rocks.

Chapter 7 describes partition of major elements and rubidium among the most important mineralogical host phases. From the discussion in this chapter it seems that Al, K, Na and Rb are concentrated mainly in aluminosilicate phases; Si in detrital quartz and authigenic chalcedony; Fe, Mn, Ca and Mg in carbonate minerals; Ti in rutile, brookite or anatase; P in Ca-phosphates.

Chapter 8 is devoted to the discussion of chemical trends in geologic history. It is concluded that variations in K, Na and Rb with time are probably caused by inherited detrital factors and thus by evolution of the earth's crust from a more mafic into a more felsic crust.

Increasing Fe and Mn content and Fe^{2+}/Fe^{3+} ratio with the age of the rocks are ascribed to the decreasing P_{O_2} in older periods of the earth's history. Increasing Mg/Ca and partly also Si/Al ratios are explained as a result of increasing P_{CO_2} with increasing age.

Chapter 9 presents discussion of Sr distribution in sedimentary carbonate rocks and its behaviour during diagenesis. It is concluded that Sr content is decreasing with an increasing degree of diagenetic alteration. The distribution of Sr in carbonate rocks is very likely bimodal (or

polymodal). This distribution is believed to be caused by original mineralogy of sediments and the type of diagenetic system. In a "closed" system of diagenesis the Sr concentrations of 600-700 ppm probably indicate an originally low-Mg calcite or aragonitic composition, whereas the Sr concentrations of about 200 ppm an originally high-Mg calcitic mineralogy.

Chapter 10 describes distribution of Sr isotopes during sedimentation and diagenesis. It is concluded that almost any secondary phenomenon would tend to increase Sr isotopic ratio and therefore the lowest value for a given suite of contemporaneous samples is the best approximation to the contemporaneous well mixed sea water.

The Sr isotopic data indicate an increasing trend from 0.7015 at 3.0 b.y. to 0.7092 for present day sea water, with clear presence of low values in Jurassic and Cretaceous, and an offset of data between 2.5 and 2.0 b.y. There are insufficient data to speculate on the more detailed fluctuations, but the general trend would be probably consistent with a predominantly mafic composition of the continental crust in Archean and continuous fractionation of a more felsic crust during younger periods.

Chapter 11 deals with utilization of Sr abundances and Sr isotopic data for recognition of carbonatites from sedimentary carbonates. It is concluded that, in general, Sr isotopic ratio below 0.707 and Sr content above 2000 ppm might serve as diagnostic features for carbonatites.

In Chapter 12 an attempted explanation of the evolution of sedimentary rocks seen in the stratigraphic record is given on the basis of the evolution of the crust for clastic rocks and P_{CO_2} and P_{O_2} for inorganic and biochemical rocks. The observed appearance of different rocks in stratigraphic record is in good agreement with predictions based on decreasing P_{CO_2} and increasing P_{O_2} in younger periods of the earth's history.

The subject of this thesis is very wide and encompassing data from very diverse fields of geology. It is therefore natural, that due to the limitations in author's knowledge, some chapters are more detailed, whereas others are possibly only a superficial discussion of the problems involved. The author would like to apologize for this uneven treatment of data, but he tried his best within the time and personal limitations imposed.

Chapter 2

STRATIGRAPHY, SEDIMENTARY PETROLOGY AND CLIMATIC INTERPRETATION

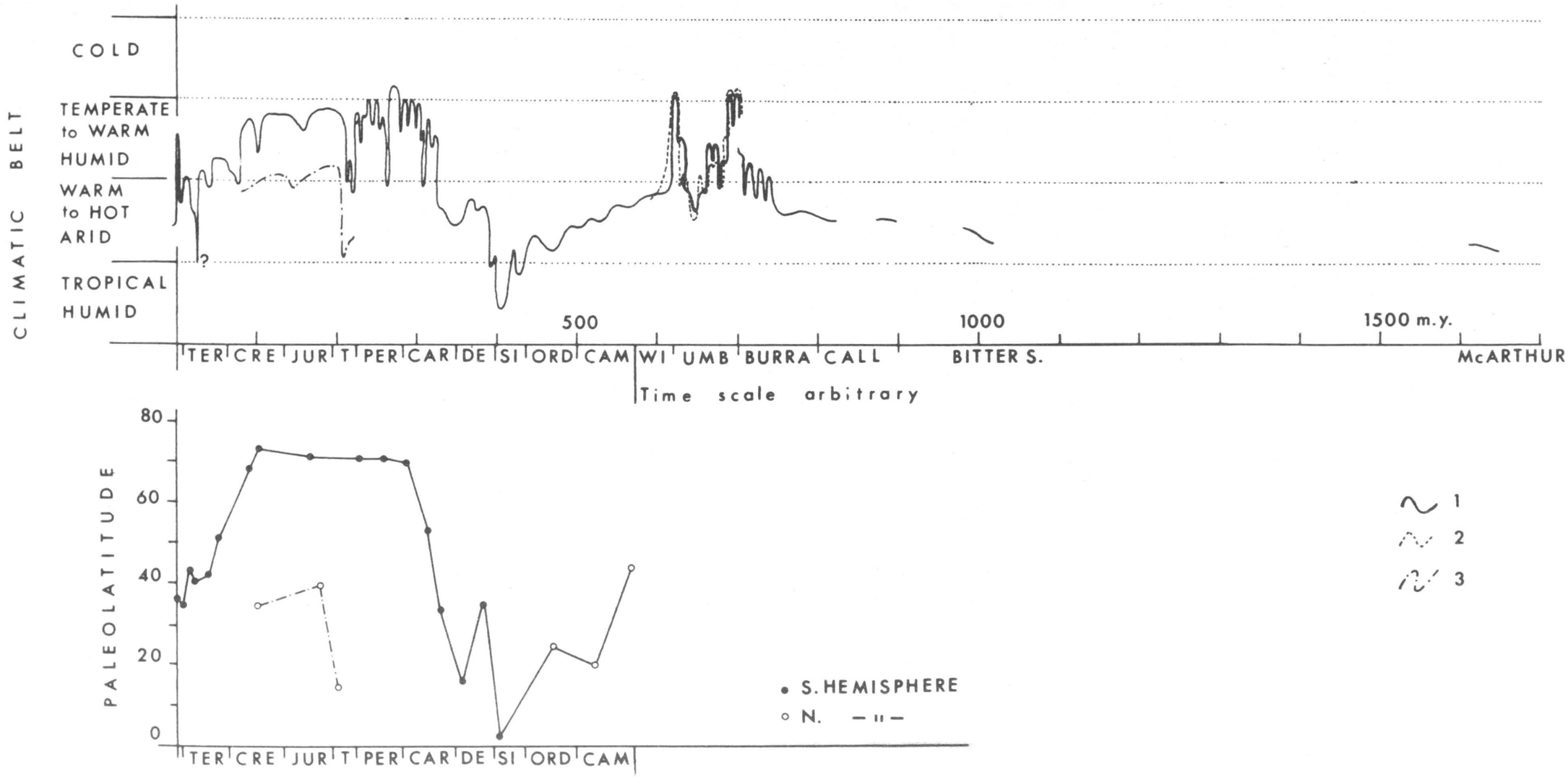
Only essential features of the stratigraphy and sedimentary petrology of the analysed carbonate sequences are given, because the wide spread in ages and localities of the samples makes detailed descriptions impossible.

The Quaternary, Paleozoic and Proterozoic samples are from Australia, a Tertiary sample from Fiji, the Mesozoic samples are from the Western Carpathians and the Archean samples are from Canada and Rhodesia. Detailed descriptions of the sequences are available in the references quoted in the text. Detailed descriptions of samples are given in Appendix 2.

The climates at the times of deposition affect the transport of elements in surface waters and their incorporation into sediments. I have used a four-fold division of climate divided into tropical humid, hot-warm arid, warm-temperate humid and cold climatic zones (fig. 1). The climatic interpretations for Australian Paleozoic are taken in part from Campbell (in Brown et al., 1968), who has been able, in most cases, to determine approximate paleotemperatures. I have tried to assign a degree of aridity or humidity where he has not already done so. Whereas the data of Campbell are based mainly on faunal and floral distribution, I have concentrated mainly on sedimentological criteria.

The interpretation of paleoclimate from sedimentological features is largely based on the rules set up by Strakhov (1967), Schwarzbach (1963) and partly Brinkman (1960). Red beds are generally believed to be sediments of a warm climate. Aridity or humidity have been inferred from their rock association (van Houten, 1961, 1964; Strakhov, 1969; McKee, 1964). The presence of early diagenetic dolomites and solution breccias ("Rauhwacken" -

Figure 1. Palaeoclimatic variations of the studied regions. The palaeolatitudes for Canberra according to Luck (1971), McElhinny and Luck (1970) and Wellman et al. (1969). The palaeolatitudes for the Western Carpathians were extrapolated from the maps of Briden and Irving (1964). Explanations:
(1) Palaeoclimatic and palaeolatitude curves for Australia.
(2) Palaeoclimatic curve for the Pertatataka and Areyonga Formations of the Amadeus Basin.
(3) Palaeoclimatic and palaeolatitude curves for the Western Carpathians.



cf. Veizer, 1970a) is interpreted as an indicator of aridity (cf. Friedman and Sanders, 1967). The dolomite/calcite ratio of landlocked or very shallow basins may also indicate a degree of aridity.

The climate can only be inferred approximately by this method, and the actual picture may be much more complicated than the pattern obtained from the limited number of data utilised. It should be noted that this interpretation assumes that the general distribution and circulation of atmosphere in geologic history followed the same rules as in the recent period (cf. Holmes, 1965 p. 743; Schwarzbach, 1963); this seems to be very probable, but it is not yet proved. Furthermore some degree of uncertainty must be introduced into paleoclimatic interpretations for the Australian continent as a whole by its size and configuration, coupled with temperature variations, relief, and the width and shape of particular climatic belts.

The situation is even more complicated for the Precambrian. Increase in P_{CO_2} and decrease in P_{O_2} (see Chapters 8 and 12) in progressively older periods would distort the whole distribution of major climatic indicators. In particular the transport of Mn and Fe would be influenced by the oxygen and CO_2 content of the atmosphere, and high P_{CO_2} in a silicate buffered ocean would cause high Mg/Ca ratios of sea water which might inhibit sulphate precipitation and enlarge the stability of dolomite at the expense of calcite etc. Absence of sulphates and salts creates problems in the interpretation of aridity. The difficulties are increased also by general lack of organisms as well as by the very low precision of stratigraphic correlations between different sequences.

For the above reasons there is a limited possibility of climatic interpretation in younger Precambrian sequences ($<$1000 m.y.). In older periods the chance of their correct interpretation is very remote and possible only under very favourable circumstances.

2.1 QUATERNARY

Two samples were collected from the Ephemeral Coorong (cf. Alderman, 1965) of the Coorong lagoon (S.A.). The sedimentation and chemistry of the water bodies and associated sediments as well as their diagenetic history are well known, and the area is regarded as a contemporaneous example of early diagenetic dolomite formation in a barred lagoonal environment with warm-hot arid climate (Skinner, 1963; von der Borch, 1965; Alderman, 1965 and others). The collected samples represent accumulation of small gastropods and silty porous bottom sediments composed from quartz and carbonate grains (mainly broken gastropods) with cryptocrystalline aragonitic contact cement.

Another sample was collected from Jay Creek (Northern Territory) on a basement formed by argillaceous rocks. It is a dark-grey nodular fine-grained limestone, known in literature as calcrete or caliche (Sanders and Friedman, 1967). This type of rocks forms crusts over the surface of semi-arid regions by capillary concentration and evaporation of sporadic rain and subsurface waters.

2.2 TERTIARY

The sample is white reef coral limestone (Futuna Limestone) from Fiji. The region is described by Ladd and Hoffmeister (1945). The limestones are underlain by lava flows dated by K-Ar method as 7-9 m.y. old and overlain by 3.5 m.y. old lavas (J.B. Gill, personal communication, 1971). This indicates their Miocene age.

2.3 CRETACEOUS

Samples No 5-7 are dark-grey to black organodetrital rocks of Early-Middle Cretaceous age (Barremian-Aptian) collected from the High Tatra Mantle Series region (Western Carpathians). Their sedimentary and/or

diagenetic environment is thought to be a deeper neritic, partly euxinic basin (Veizer, 1968b; Veizer and Demovic, in press). This environment is indicated by the association of organisms, with neritic and pelagic elements, black colour caused by high content of unoxidised organic matter and high Sr content. The geology and stratigraphy of the region have been described by Kotański (1961), Gorek and Veizer (1965) and Veizer (1968a,b, 1970b).

Samples 8-9 are typical hemipelagic-pelagic limestones. They are very similar to the well known Biancone Limestones of the Alps (cf. Aubouin, 1965). The prevailing microfacial association is Calpionella-Radiolaria with less abundant Nannoconus. Their geology and petrology have been described by Andrusov (1964), Misík (1966), Mahel and Buday (1968) and others.

The prevailing climatic conditions during Early and Middle Cretaceous, for the W. Carpathians area, were temperate and humid (Veizer, 1968b; Veizer and Demovic, in press).

2.4 JURASSIC

Samples 10-12 are massive muddy hemipelagic limestones of Malmian age with predominantly Globochaeta-"Halobia", "Protoglobigerina", Calpionella and "Saccocoma" microfacies (Kotański, 1961; Veizer, 1968a,b; Veizer and Demovic, in press). Sample 13 represents deep water pelagic rock associated with radiolarites. This type of rock was common in deep troughs, whereas the rocks of the type 10-12 were deposited on shallower ridge areas (Andrusov, 1964; Misík, 1966; Mahel and Buday, 1968).

Samples 14-16 are shallow neritic crinoidal limestones composed almost completely from crinoidal ossicles and cemented by sparry calcite. Their high sorting indicates accumulation by bottom currents or deposition in a high energy environment (Kotański, 1961; Veizer, 1968a,b; Veizer and Demovic, in press).

The Jurassic climate of the W. Carpathians was mainly of warm to temperate humid type. Increased aridity and temperature was observed only during Early Malmian period (Veizer, 1968b; Veizer and Demovič, in press).

2.5 TRIASSIC

Petrological description and environmental interpretation of the West Carpathian Triassic rocks, as well as their diagenetic history have been discussed in detail by Veizer (1970a). The general geology of the area can be found in Andrusov (1964) and Mahel' and Buday (1968), the stratigraphy in Bystrický (1967), and the microfacial description in Misík (1966).

In general there is a lateral change from nearshore "hypersaline", in part lagoonal, sequences in the north into a belt of late diagenetic dolomites and finally organodetrital, mainly algal, bank limestones in the south. The position of the Triassic samples may be easily traced in Veizer's (1970a) data.

The climate during Scythian-Norian period was of a warm to hot arid type, whereas a humid warm to temperate climate was typical for Rhaetian period.

2.6 PERMIAN

The Permian samples were marine facies brachiopods collected predominantly from shale sequences. Their facies description is given below.

The Gerringong Volcanics (N.S.W.) of Kazanian age are submarine lava flows interbedded with marine sediments (Raam, in Packham, 1969).

The Tiverton Formation (Qld.) of Late Artinskian age comprises mainly ferrugineous sandstones, lithic sandstones, calcareous siltstones and

coquinite (Jensen et al., 1966).

The Cattle Creek Formation (Qld.) of Early to Middle Artinskian age is composed mainly of shales, but sandstones and limestones are also present. The formation contains also evaporites and glacial erratics (Campbell et al., in Hill and Denmead, 1960).

Climate during Permian period was predominantly of temperate to cool humid type as evidenced by coal measures, glacial sediments, iron concretions and general lack of carbonates and evaporites. This conclusion is supported also by faunal distribution (Campbell, in Brown et al., 1968) and by palaeomagnetic data (Irving, 1964, McElhinny and Luck, 1970).

On the other hand, the Cattle Creek Formation and several other contemporaneous units of Queensland (Campbell, in Hill and Denmead, 1960) contain climatically "incompatible" rock associations, with evaporites, glacial erratics and carbonates. The glacial erratics are probably allochthonous, whereas the evaporites and carbonates are autochthonous, and indicate at least a temperate, semi-arid climate during their deposition. The occurrence of evaporites of similar age in the Perth basin (Campbell, in Brown et al., 1968) supports this. The erratics might be regarded as elements reworked from older Carboniferous or Permian sediments.

This conclusion is difficult to reconcile with the geographic position of Australia inferred from the paleomagnetic data (McElhinny and Luck, 1970). It also creates some problems in view of the generally accepted type of glaciation. The evidence for glaciation in many areas, the extensive lateral presence of tillites and varves in places which had small relief during the Permian, and the existence of glacial products in marine sequences led Campbell (in Brown et al., 1968) to conclude that the glaciation was of a continental type. However, Strakhov (1967) regarded this glaciation as of the alpine type because of the simultaneous presence of evaporites. The

inference by Campbell of several stadials and/or glacials (Sakmarian?, Early Artinskian-Kungurian?) and interstadials and/or interglacials (Artinskian?, Kazanian?, Tatarian?) may help to resolve at least some part of this controversy. However it is quite possible that the vertical relief was responsible for preservation of the ice sheets during warmer periods. The data of Crowell and Frakes (1971) support this view. In their interpretation, the continental glaciation was limited to the uppermost Stephanian (Carboniferous) and Sakmarian (lowermost Permian). All preceding and succeeding glacial occurrences were limited to the alpine environment.

2.7 CARBONIFEROUS

Sequences from which the Carboniferous marine brachiopods were collected are described below.

The Levipustula Beds (Buckets Gap Formation, N.S.W.) of Westphalian age consists mainly of mudstones and siltstones with abundant carbonaceous material (Engel et al., in Packham, 1969).

The Late Visean Wallaringa Formation (N.S.W.) (Engel et al., in Packham, 1969) is composed mainly of coarse tuffaceous sandstones and polymictic conglomerates. It also contains red beds, arenites and shales. The formation is regarded as being largely of the Piedmont type.

The underlying Late Visean Wirragulla Beds are marine, shallow water, buff-coloured siltstones and lithic sandstones (Campbell, in Packham, 1969).

The Tournaisian limestone of the Bonaparte Gulf Basin (W.A.) represents organodetrital reef-like facies (Veevers and Roberts, 1968; Veevers, 1969a,b).

From the faunal and sedimentological evidence (Campbell, in Brown et al., 1968) it seems probable that the climate during Early Carboniferous was of a warm semi-arid to arid type. According to the same author Late Carboniferous is dominated by temperate to cool climate (lack of carbonates, glaciation),

most probably of a humid type (coal formations). The above climatic evolution is in good agreement with palaeomagnetic data (McElhinny and Luck, 1970). The existence, in Canning Basin, of dolomites and anhydrites of possible Wesphalian age (Campbell, in Brown et al., 1968) would indicate a short incursion of a warm-temperate semi-arid climate as in the Permian.

2.8 DEVONIAN

The Late Devonian carbonate sequence of the Bonaparte Gulf Basin (W.A.) represents predominantly algal and partly stromatolitic fore-reef and reef limestones. The formation was deposited in a shallow warm sea (Veevers and Roberts, 1968; Veevers, 1969a,b).

The Cavan Bluff Limestones (Emsian) of the Murrumbidgee Group (N.S.W.) are sediments of an intertidal to very shallow shelf sea environment as indicated by the presence of stromatolites and mud cracks (cf. Packham, 1969; Campbell, in Brown et al., 1968).

The climate during deposition of the Late Devonian Bonaparte Gulf Basin was probably of a warm to temperate (reef development) and of semi-arid to arid nature as indicated by dolomites and red sandstones and shales of the Cockatoo Formation (cf. Veevers and Roberts, 1968). The Murrumbidgee Series with its carbonate succession and very common red beds suggests similar climatic conditions also during the late Middle and Upper Devonian. This conclusion is in agreement with the nature of the climate inferred from floral and faunal distribution (Campbell, in Brown et al., 1968) as well as with the palaeomagnetic data (McElhinny and Luck, 1970).

2.9 SILURIAN

The Hume Series of the Yass (N.S.W.) Silurian sequence, from which all samples were collected, is described by Packham (1969). In a more recent

subdivision of Link (1970), the lower part of the collected sequence was attributed to the Huttons Corner Group, and the sample No. 63 to the base of the Booroo Ponds Group (former Lower Trilobite Bed). The age of the sampled sequence is Early and Middle Ludlovian (Link, 1970).

The sequence represents alternation of shales, siltstones and limestones of biohermal and organodetrital types. The biohermal limestones (No. 64, 65, 67 and partly 68) are sediments of a warm shallow sea with moderate to high energy of their sedimentary environment. The other samples are black organodetrital limestones of micritic types (particularly No. 63). They display some features of a stagnant low energy and low Eh environment as indicated by their textures, organic matter content, pyrite grains and association with dark shales. This would indicate their deposition and/or diagenetic alteration in a semi-barred basin of a partly euxinic type for the latter.

The presence of bioherms and biostromes throughout the whole East Coast would indicate a warm to hot tropical climate (cf. Campbell, in Brown et al., 1968) for almost the whole Silurian period.

Presence of low grade Mn ores and Fe concentrations in the Silurian sequence of the northern parts of the New England geosyncline (cf. Campbell, in Brown et al., 1968; Voisey, in Packham, 1969) together with much smaller abundance of evaporites, dolomites and associated red beds compared to the Devonian or Ordovician sequences are consistent with a generally humid character of the climate.

On the other hand, presence of dolomite-limestone-anhydrite sequence in Wenlockian of Perth and Carnavon Basins, inorganic limestones in Yass region of the same age and fluvial-aeolian sands with halite pseudomorphs of probable Silurian age in Amadeus basin (cf. Campbell, in Brown et al., 1968) requires increased aridity at least during certain intervals of the

Silurian period. The conclusion that the Silurian climate was predominantly warm to hot and humid is supported also by the geographic position of Australia as inferred from palaeomagnetic data (McElhinny and Luck, 1970).

2.10 ORDOVICIAN

The Ordovician samples are from Gordon Limestones of Tasmania. According to Banks (in Spry and Banks, 1962) and Colbert (personal communication, 1970) this formation is about 5000 feet thick, and is of Late Canadian (Late Arenigian) to Late Ordovician age. The limestone is a pure bedded calcilutite with some calcarenite and a few beds of boulder calcirudite. Arenaceous and argillaceous limestones are more common near the base and near the top of the formation.

Banks (ibidem) describes sponges, stromatoporoids, tabulate and rugose corals, polyzoa, brachiopods, pelecypods, gastropods, cephalopoda, trilobites, ostracods, echinoderms, graptolites and algae from the limestones. However, the majority of the samples contain black carbonate mud, without or with very small contents of organisms. The black colour is caused by very high contents of unoxidised organic matter together with nodules and spherulites of pyrite, chalcopyrite and sphalerite of probable syngenetic origin (cf. Banks, in Spry and Banks, 1962) and strongly suggests an euxinic sedimentary and diagenetic environment.

It is my belief that carbonate muds of this type are formed by combined biochemical (predominantly bacterial) and inorganic precipitation and/or diagenetic alteration in warm semi-barred basins of partly euxinic type (Veizer, 1970a). This remark applies also to the part of the Silurian sequence described previously.

For the reasons stated by Campbell (in Brown et al., 1968) the climate during the Ordovician period was warm to hot. I wish to stress the aridity

of the climate as indicated by the frequent presence of dolomite in carbonate sequences, their association with red beds and the presence of gypsiferous layers and halite casts in the Georgina, Amadeus and Canning Basins (cf. also Campbell, ibidem). This type of climate probably persisted throughout the most of the Ordovician period. The data are again in good agreement with the palaeomagnetic interpretations of McElhinny and Luck (1970).

2.11 CAMBRIAN

The Cambrian sequences collected in the Amadeus Basin (N.T.) were the Goyder Formation (early to middle Late Cambrian), the Jay Creek Limestone (early Middle to early Late Cambrian) and the Hugh River Shale (early Middle Cambrian). The geology and petrology of the region are described by Wells et al. (1970).

According to these authors, the Goyder Formation is composed of sandstones and siltstones with interbedded dolomites and limestones. The limestones are mainly oolitic with cross lamination and intraformational breccias. Arenaceous dolomites are also present. The collected samples are predominantly of oomicrite to micrite types and are associated with red beds.

The Jay Creek Limestone sequence is composed from yellow-brown to grey, thick bedded, fine to medium-grained limestones, which are commonly algal and oolitic. The limestones are interbedded with red siltstone and rare sandstones. The sequence also contains solution breccias ("Rauhwacken" - cf. Veizer, 1970a).

The Hugh River Shale sequence is predominantly red-brown and grey-brown siltstone and shale. The base is formed by ~100 feet of siltstone and chert and the next 100 feet are calcitic dolomites, shales, siltstones and minor

sandstone. The limestones are predominantly of micrite algal type and the dolomites are of early diagenetic type (see Appendix 2).

The collected Middle Cambrian sequences of the Georgina Basin (N.T. and Qld.) are described as follows:

The Quita Formation (Qld.) is a calcareous formation of hard flaggy limestone banks interbedded with marly and sandy beds (Hill and Denmead, 1960).

The Currant Bush Limestone (Qld.) is contemporaneous with the Quita Formation. The sequence is formed predominantly by bituminous, flaggy limestone with oolitic, shaly and marly interbeds (Hill and Denmead, 1960). The collected samples represent late diagenetic dolomites.

The Thorntonia Limestone (Qld.) is composed predominantly of dolomitic limestones, dolomites and limestones with chert layers and nodules (Hill and Denmead, 1960). The collected samples are early and late diagenetic dolomites.

The Montejini Limestone (N.T.) is probably originally an aragonitic calcilutite (Brown, 1968). The collected samples are dolomitized microcrystalline limestones.

The Flinders Ranges (S.A.) suite comprises Middle Cambrian Wirrealpa Limestone, and Lower Cambrian Pararra and Wilkawillina Limestones.

The Wirrealpa and Wilkawillina Limestones are predominantly of reef-like (Archaeocyatha) or reef-detrital types. The Pararra Limestone is a deeper basinal facies, slightly younger or contemporaneous with the Wilkawillina Limestone (cf. Wopfner in Parkin et al., 1969).

In general, the majority of sequences represent intertidal to shallow subtidal facies. They may be sediments of several transgressive and regressive periods over a peneplained basement. An impression of the general palaeogeography can be found in Brown (1968) and Campbell (in Brown

et al., 1968).

The description of sequences indicates persistence of a hot-warm arid climate during major part of the Cambrian period. This is clearly indicated by the dolomite/limestone ratio, the presence of carbonate-red beds association, the presence of early diagenetic dolomites and "Rauhwacken" and also by the existence of salt pseudomorphs and gypsum (cf. Campbell, ibidem). This is also in agreement with the faunal distribution (Campbell, in Brown et al., 1968) and paleomagnetic data of McElhinny and Luck (1970) and Luck (1971), with the possible exception for Early Cambrian period.

2.12 COMMENT ON AUSTRALIAN CLIMATE DURING PALEOZOIC

From the above data it seems likely that, throughout the major part of the Paleozoic, the western part of Australian continent displayed a slightly higher degree of aridity and higher temperature than the eastern part. If true, this might be caused by tectono-sedimentary factors (deeper marginal basins in the east vs. stable platform in the west), tectono-climatic factors (high mountains causing higher precipitation vs. stable platform), or the internal position of the western part within the former Gondwana continent. It is possible that the tectono-sedimentary factors played an important role during the Early Paleozoic, whereas the tectono-climatic ones were important during the Late Paleozoic. These factors together with the large size of the Australian continent, might also account for the pronounced local nature of climate and its variations.

2.13 PRECAMBRIAN

2.13.1 Flinders Ranges (South Australia)

The Adelaidean Precambrian sequence is well known and well described in the literature. The most recent and possibly most comprehensive review was published by Thomson (in Parkin et al., 1969).

The youngest group of the Adelaidean system, the Wilpena Group, consists predominantly of shallow water marine and lagoonal red beds and carbonates. The collected samples are micritic limestone of the Wonoka Formation, and early diagenetic dolomite of the Nuccaleena Formation.

The older Umberatana Group according to Thomson (ibidem), consists of four main subgroups, the Yerelina Subgroup (containing tillites), the interglacial Willochra and Farina Subgroups and the lower glacial Yudnamutana Subgroup. The interrelations of different facies are summarised in Parkin et al. (1969, p. 64). Samples were collected from the following rock units:

The Willochra Formation, which is composed mainly of shallow water or lagoonal red beds and carbonates. The collected samples are dolomitic siltstone and stromatolitic limestone.

The Trezona Formation, composed of silicified stromatolitic limestones intercalated with grey marls with ripple marks, sun cracks, and rain drop structures.

The Etina Limestone, predominantly arenaceous oolitic and algal limestone. The sequence grades laterally into red beds of the Willochra Formation.

The Brighton Limestone, composed in its lower part from dark dolomitic and oolitic, partly algal limestones. The upper part contains variegated limestones and siltstones. It seems that this Formation is of subtidal shallow water origin at the base, whereas the upper part might be partly of intertidal to lagoonal origin.

The Tapley Hill Formation, composed of laminated dark shales and calcareous siltstones of a shallow marine environment.

The Tindelpina Shale Member, a dark grey finely laminated shale unit with thin layers of early diagenetic dolomites.

The Yudnamutana Subgroup, of which the Appila Tillite is a member, comprises tillitic sequences with shales, siltstones, sandstones and includes the Holowilena and Braemar sedimentary iron formations. According to Thomson, the subgroup was deposited in a shallow epicontinental sea.

The Burra Group, underlying the Umberatana Group, is at the base formed predominantly of sandstones, red beds and early diagenetic dolomites. The upper part is formed of black cherts, laminated siltstones and mudstones and black dolomites. The Auburn Dolomite and its time equivalents are within the middle part, whereas the Skillogalee Dolomite represents the lower part of the group. The latter commonly contains sedimentary magnesite, ripple marks, sun cracks, salt casts and intercalations of "Rauhwacken". Algal structures are generally silicified.

The River Wakefield Group (equivalent of the Upper Callanna Beds) is formed by 7000 feet of grey siltstones, early diagenetic dolomites with black cherts and pale sandstones.

The stratigraphy of the whole Adelaidean Supergroup is uncertain. On the basis of radiometric data Compston et al. (1966) assigned an age of 850 $\pm$ 50 m.y. to the Wooltana Volcanics, which being part of the (oldest) Callanna Beds, underlie most of the sedimentary sequence. As the volcanics are metamorphosed the age is regarded only as a younger limit. Cooper and Compston (1971) dated the amphibolite facies metamorphic basement of the Houghton inlier near Adelaide at 867 $\pm$ 32 m.y. Because the overlying Burra Group is not affected by this metamorphism, it should be younger than this estimate. The upper part of the River Wakefield Group

seems to interfinger with Rhynie Sandstones of the Burra Group (Thomson, in Parkin et al., 1969). This would indicate a similar or slightly older age (≲900 m.y.) for the River Wakefield Group.

The radiometric determinations as interpreted above indicate a younger age for the base of the Adelaidean Supergroup than was suggested by Glaessner et al. (1969) on the basis of stromatolites, and do not support the correlation of the Wooltana with the Roopena Volcanics. Nevertheless, reasonable doubts remain, and it is possible for example that the Callanna Beds may be as old as 1300 m.y.

The samples collected are predominantly sediments of lagoonal, intertidal or shallow subtidal environments as indicated by stromatolites, early diagenetic dolomites, red beds, mud cracks, sedimentary magnesite, salt casts, ripple marks etc. (cf. Veizer, 1970a). Laminated calcareous or dolomitic siltstones and mudstones are most probably sediments of shallow epicontinental seas.

The problems of palaeoclimatological interpretation in the Precambrian were discussed in the introductory part of this chapter. Nevertheless the interpretation for this supergroup should be quite reliable.

The Wilpena Group as a whole may be regarded as sediments of a warm-hot arid climate as indicated by the predominant red beds + carbonate (often early diagenetic dolomites) association.

The Umberatana Group consists from two glacio-marine tillitic sequences at the base and the top of the group. These tillites are well known and their detail discussion is above the scope of this thesis. The existence of sedimentary ironstones indicates temperate humid climate for a part of the basal tillitic sequence (Yudnamutana Subgroup).

Laminated calcareous siltstone sequences (Tindelpina Shale Member, Tapley Hill Formation, Enorama Shale etc.) are regarded as predominantly

sediments of a temperate humid zone for two reasons.

(a) The rocks always underlie or overlie the tillitic sequences.

(b) In my view the distinct lamination is best explained by a climatic factor, probably of a seasonal nature.

The rocks could be then regarded as an equivalent of the well known varvitic sequences of Scandinavia. The problem of lamination is discussed in detail by Schwarzbach (1963).

The Brighton Limestone and the major part of the Willochra Subgroup are characterised by similar features as Wilpena Group indicating their deposition in a warm arid climate.

The Burra Group and both the Lower and Upper Callanna Beds (River Wakefield Group) show distinctive features of a hot-warm arid climate (cf. Thomson, in Parkin et al., 1969; Veizer, 1970a). Partial exception from this general pattern are laminated sequences of the upper part of the Burra Group (Belair Subgroup and partly Saddleworth Formation), which are regarded as sediments of a warm-temperate humid climate for the reasons stated previously.

2.13.2 Amadeus Basin (Northern Territory)

The Proterozoic sedimentary suite from this region comprises the Pertatataka, Areyonga and Bitter Springs Formations and Heavitree Quartzite (Wells et al., 1970).

The youngest Pertatataka Formation is composed of several members with different lithology and origin. The samples collected are from the youngest, the Julie Member, which is a sequence of dolomites, limestones, siltstones and sandstones. The dolomites are thick-bedded and massive, medium to coarse grained, oolitic and sandy. They are predominantly of early diagenetic origin and alternate with red beds and layers of "Rauhwacken".

The Bitter Springs Formation is subdivided into the basal Gillen Member and overlying Loves Creek Member. The Gillen Member is composed mainly of early diagenetic dolomites with subordinate sandstones, siltstones and shales of the red bed type. The sequence contains common pseudomorphs after halite, as well as gypsum and salt layers. The gypsum and salt layers are to my knowledge the oldest or second oldest (after the Grenville Formation of N. America) known gypsiferous evaporites as yet known in the world. The Loves Creek Member comprises mostly siltstones with interbeds of cherts, early diagenetic dolomites and rare sandstones. The detrital rocks are of the red bed type. Dolomites are algal, yellowish-brown, laminated and fine-grained with chert nodules. Limestones are dark-grey, cavernous with nodules of chert.

The association of rocks in the Julie Member of the Pertatataka Formation as well as in the Bitter Springs Formation is typical of very shallow water, subtidal, intertidal and lagoonal environments in a hot arid climate. This conclusion is corroborated also by structural features such as mud cracks, ripple marks, presence of "Rauhwacken", limonitic concretions and crusts, evaporites and stromatolites.

Rb-Sr dating of shales from the Pertatataka Formation (from older members than the Julie Member) indicates apparent ages of 760 and 822 m.y. (Bofinger, in Wells et al., 1970). A total rock shale age of 730 m.y. was reported by Compston and Taylor (1969) for the Winnall Beds, which are lateral equivalent of the Pertatataka Formation. Although the meaning of Rb-Sr apparent ages of shales is not yet clear, the available data would indicate an age between Cambrian and 800 m.y. for the Pertatataka Formation.

In spite of doubts concerning the time correlation of tillites (Crawford and Daily, 1971), it is very probable that over short distances such correlation may be valid. It seems reasonable to relate the two

tillitic sequences of the Amadeus Basin (Areyonga Formation and Olympic Member of the Pertatataka Formation) with the Yudnamutana and Yerelina Subgroups of the Flinders Ranges. Any more detailed correlation is unwarranted in view of the uncertainty in dating of both regions.

Rb-Sr dating of shales from the Bitter Springs Formation indicated an apparent age of 1170 m.y. (Bofinger, in Wells et al., 1970). Cooper et al. (1971) found a minimum age of 1280 m.y. for the Truer Member of the Vaughan Springs Quartzite of the adjoining Ngalia Basin. The latter is generally correlated with the Heavitree Quartzite of the Amadeus Basin (Wells et al., 1968). Since the Heavitree Quartzite is underlying the Bitter Springs Formation, the data would indicate an age of about 1000-1200 m.y. for the latter. Equivalents of acid volcanics underlying the Dean Quartzite (equivalent of Heavitree Quartzite) were dated as 1150 m.y. old (Gray, 1971). This would indicate the lower limit (1000 m.y.) as the more probable age for the Bitter Springs Formation. These data do not agree completely with the stratigraphy proposed on the basis of stromatolites by Glaessner et al. (1969), which indicated an Upper Riphean (650-950 m.y.) age for the Bitter Springs Formation. On the other hand the data are in agreement with the correlation chart of Dunn et al. (1966).

2.13.3 Tasmania

The Precambrian sequence of Tasmania is described by Spry (in Spry and Banks, 1962). The younger unmetamorphosed sedimentary rocks are correlated tentatively with Carpentarian by Crook (in Brown et al., 1968), but their age is uncertain. The sample analysed is a black fine-grained argillaceous limestone of probable Adelaidean age (Colbert, personal communication, 1970).

2.13.4 Hamersley Range Area (Western Australia)

According to Daniels (1966) the Proterozoic suite of this region comprises, from the bottom to the top, the Mt. Bruce Supergroup (composed

tillitic sequences of the Amadeus Basin (Areyonga Formation and Olympic Member of the Pertatataka Formation) with the Yudnamutana and Yerelina Subgroups of the Flinders Ranges. Any more detailed correlation is unwarranted in view of the uncertainty in dating of both regions.

Rb-Sr dating of shales from the Bitter Springs Formation indicated an apparent age of 1170 m.y. (Bofinger, in Wells et al., 1970). Cooper et al. (1971) found a minimum age of 1280 m.y. for the Truer Member of the Vaughan Springs Quartzite of the adjoining Ngalia Basin. The latter is generally correlated with the Heavitree Quartzite of the Amadeus Basin (Wells et al., 1968). Since the Heavitree Quartzite is underlying the Bitter Springs Formation, the data would indicate an age of about 1000-1200 m.y. for the latter. Equivalents of acid volcanics underlying the Dean Quartzite (equivalent of Heavitree Quartzite) were dated as 1150 m.y. old (Gray, 1971). This would indicate the lower limit (1000 m.y.) as the more probable age for the Bitter Springs Formation. These data do not agree completely with the stratigraphy proposed on the basis of stromatolites by Glaessner et al. (1969), which indicated an Upper Riphean (650-950 m.y.) age for the Bitter Springs Formation. On the other hand the data are in agreement with the correlation chart of Dunn et al. (1966).

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2.13.4 Hamersley Range Area (Western Australia)

According to Daniels (1966) the Proterozoic suite of this region comprises, from the bottom to the top, the Mt. Bruce Supergroup (composed

of the Fortescue, Hamersley and Wyloo Groups), the Bresnahan Group and the Bangemall Group.

Bangemall Group

The upper part of the sequence (Daniels, 1966) is composed predominantly of quartzites and shales (Kurabuka Formation and Fords Creek Shale). The oldest unit, from which the samples were collected, is the Top Camp Dolomite. The dolomite is grey, fine-grained, partly recrystallised and most probably of early diagenetic origin. Stromatolites were observed within the dolomites and intercalations of quartzites and shales are also common. There are slight unconformities within the sequence. The dolomite was very likely deposited in a shallow subtidal or intertidal environment of a semi-barred basin or lagoon.

The younger sediments of the group contain manganese-bearing shales and dolomites and grade lateraly into the manganese province of the Oakover-Davis Basin (MacLeod, 1966). Although most of the Mn localities are secondary (de la Hunty, 1963), syngenetic Mn content of the shales is as high as 13%.

This creates some problems in climatic interpretation of aridity or humidity. The climate during deposition of the Bangemall Group was probably warm. Existence of early diagenetic dolomites would demand an arid climate, whereas the high Mn concentration would require humidity. Although it is true that the dolomite is less abundant in the upper part and Mn in the lower part of the group, so that there might have been a change from a warm arid to a warm humid climate, the interpretation is strongly dependent on the P_{O_2} and P_{CO_2} level of the contemporaneous atmosphere. This would influence the transport of Mn as well as its separation from Fe. At present no firm conclusion can be reached, since the composition of the atmosphere is not known.

Radiometric dating indicates an age between 1000 and 1100 m.y. for this group (Compston and Arriens, 1968). The upper limit is preferred by Trendall and Blockley (1970).

Mt. Bruce Supergroup

The geology and stratigraphy of this supergroup is described in detail by several authors (Daniels, 1966; MacLeod, 1966; Trendall and Blockley, 1970 and others), as it contains one of the biggest banded iron formations of the world.

The youngest Wyloo Group is composed mainly of clastics and some carbonates of a marginal trough basin, the middle Hamersley Group contains predominantly chemical sediments with banded iron ore formations, and the oldest Fortescue Group comprises mainly volcanic and detrital formations. For the details of stratigraphy and petrology see monographs of MacLeod (1966) and Trendall and Blockley (1970).

The Duck Creek Dolomite (Wyloo Group) is a thickly bedded brownish grey rock with numerous chert bands and algal structures. The dolomite is of early diagenetic origin or possibly even a primary precipitate.

The Wittenoom Dolomite (Hamersley Group) in its lower part is mainly massive, medium to thin bedded dolomite with rare black cherts. The dolomite is finely crystalline, of brown, pink and grey colours, often laminated (banded) without fossil structures. It is either of early diagenetic origin or a primary precipitate. In its upper part the sequence contains increasing amount of shale, chert and iron layers.

The sample of Pillingani Tuff (Fortescue Group) is dark grey to black, fine grained, stromatolitic, marly silicite.

The age of the Mt. Bruce Supergroup is between 1950-2240 m.y. (Compston and Arriens, 1968). Trendall and Blockley (1970) prefer an age of about 2200 m.y. for the Fortescue Group, 2000 m.y. for the Hamersley

Group and between 2000-1700 m.y. for the Wyloo Group.

The origin of Precambrian iron ore formations and their associated sediments has long been a subject of controversy and is beyond the scope of this work (see Strakhov, 1969; James, 1966; Lepp and Goldich, 1964; Borchert, 1966; Trendall, 1968; Trendall and Blockley, 1970; Fuchtbauer and Muller, 1970 and others). In general there is some agreement that the ores are chemical and/or colloidal precipitates, deposited offshore in shallow marine basins. The association of rocks within the supergroup would be compatible with such an interpretation.

The problem of a climatic interpretation was already discussed in the Bangemall Group sediments. The difficulties mentioned are even more pronounced during sedimentation of the Mt. Bruce Supergroup because of its much greater antiquity.

2.13.5 McArthur Basin (Northern Territory)

According to Crook (in Brown et al., 1968) the major part of the McArthur Group was deposited unconformably on the Tawallah Group, which consists largely of arenaceous clastics and volcanics. These two groups define together the "Carpentarian" System. The McArthur Group comprises predominantly dolomites and shales whereas the overlying Roper Group is dominated by clastics.

Stratigraphy and sedimentary petrology of the part of the McArthur Group from which the samples were collected (Bauhinia Downs), is described in detail in Plumb and Brown (in press). Numerous additional data were made available to me by M.C. Brown in personal communication. The sequence in general represents one transgressive and regressive cycle.

The Reward Dolomite is mainly dololutite and pelletal or intraclastic dolarenite with abundant stromatolitic structures and chert nodules. The dolomites are interbedded with dolomitic shales, K-rich mudstones,

breccias and dolomitic sandstones with crossbedding and ripple lamination. The rocks are sediments of shallow water to intertidal environment deposited during a regressive cycle.

The Cooley Member consists predominantly of clean fine-grained to massive dolomite and is believed to be either a carbonate reef laterally equivalent to the pyritic shales of the HYC Member of the Barney Creek Formation, or an upper part of the Mitchell Yard Member. Some dololutites contain radiating aggregates of hexagonal "needles". According to Brown (personal communication, 1971) these structures are pseudomorphs after aragonite.

The Mitchell Yard Member of the Emmerugga Dolomite consists mainly of clean, thick bedded dololutite generally without stromatolites or chert nodules. Stromatolites, shaly beds (red beds with halite casts), oolitic and intraclastic dolarenites, dolomitic breccias, dolomitic sandstones and dolarenites with cross bedding, ripple marks and current laminations are present as rare intercalations. The sequence represents sediments of a shallow marine, subtidal and intertidal environments.

The Mara Member of the Emmerugga Dolomite consists mainly from cherty dololutite with abundant algal stromatolites. Interbeds of dolomitic siltstones and silty dololutites with halite casts, dolomitic breccias, oolitic dolarenites and chert free clean dololutites are also present. The sequence was deposited probably in a shallow marine or lagoonal predominantly intertidal and subtidal environment.

The Leila Sandstone (Tooganinie Formation) is red dolomitic sandstone grading lateraly and verticaly into red dolomitic siltstones of the Myrtle Creek Shale Member. This subaerial red beds contain also intercalations of pure and silty dololutites with halite casts and solution breccias. The collected sample is fine grained laminated arenaceous early diagenetic

dolomite with rare oolithes.

Although this sequence is very old, the presence of "collapse breccias", salt casts and general lithology (red beds and early diagenetic dolomites) strongly indicates warm to hot arid climatic conditions. The red beds (Myrtle Creek Shale) represent one of the oldest known unquestionable occurrences of red beds in the world.

The K-Ar and Rb-Sr dating of glauconites indicated a minimum apparent age of 1400 m.y. for the Roper Group and 1600 m.y. for the Tawallah Group (McDougall et al., 1965 and Compston and Arriens, 1968). Richards (1963) gave a model Pb age of 1560 m.y. for the Amelia Dolomite of the McArthur Group. One total rock shale isochron for the Mullera Formation (South Nicholson Basin), which is correlated with the Roper Group, produced an apparent age of 1510 $\pm$ 120 m.y. (R.R. Harding, in Compston and Arriens, 1968). The above interpretation of ages would possibly limit the age of the McArthur Group to 1500-1600 m.y. bracket, although the uncertainties involved in the age interpretations are considerable.

2.13.6 Steep Rock Lake Group (Ontario, Canada)

According to Jolliffe (1966), this group was deposited on an eroded granitic basement and is composed of a Conglomerate Formation, succeeded by Dolomite, Orezone and Ashrock Formations. An erosional disconformity separates the Dolomite and Orezone Formation.

The Dolomite Formation shows well defined beds with little evidence of recrystallization. The limestones and dolomites are greyish and very fine grained with significant content of Fe and Mn and are interbanded with cherts. They also contain structures of possible organic origin.

The Orezone Formation according to Jolliffe (1966) is an ancient Archean soil profile with Mn and Fe oxides and ferrugineous bauxite. If true, this might be the oldest known bauxite and possibly even soil

profile known in the world. The association of the rocks of the Orezone Formation, in an atmosphere containing free oxygen, would indicate a humid warm to hot climate; however due to the large uncertainties in our knowledge of the composition of the Archean atmosphere and hydrosphere, the data are inconclusive.

The Steep Rock Lake Group is older than Kenoran Orogeny, which is about 2500 m.y. old (Jolliffe, 1966). According to Lepp and Goldich (1964) the age of the iron ore formation is about 2600 m.y.

2.13.7 Bulawayan System (Rhodesia)

The Bulawayan System is composed predominantly of basic lavas and minor sediments. The Zwankendaba Group (MacGregor, 1940) of this system comprises dolomitic and calcareous beds associated with banded ironstones, arkoses and conglomerates incorporated in considerable thickness of volcanic greenstones. The whole sequence is subjected to a very low degree of metamorphism.

The limestone is coloured light-grey to black with veins of dolomites in some places. Dolomite, with exception of the Huntsman Lime Quarry, is common along the whole strike of the carbonate outcrops. The limestones contain substantial amount of graphite and sometimes also bands of cherts. They also contain structures formed by organisms (probably algae), which are as yet the oldest or second oldest known in the world (cf. Engel et al., 1968).

Depositional environment of this suite seems to be different from all previously discussed environments. In the Bulawayan System the rocks are surrounded by massive basic lavas without any apparent sialic basement, whereas in all the other cases (except for the pelagic rocks) the rocks are sediments of shallow epicontinental seas which are transgressive over older sialic basements. The Bulawayan sedimentary environment may to some

extent resemble the recent island arcs.

According to Vail and Dodson (1969) the Bulawayan System is between 3300-3000 m.y. (using $\lambda = 1.39 \times 10^{-11}$) or 3100-2810 m.y. (using $\lambda = 1.47 \times 10^{-11}$) old. This age is indicated by K-Ar and Rb-Sr data on pre- and post-Bulawayan granites and granitic gneisses. As there are no isochron data available, the above ages should be regarded as minimum estimates (Vail and Dodson, 1969).

2.14 PALAEOCLIMATIC CONCLUSIONS

As seen from fig. 1 the Australian curve indicates general cooling of climate from Quaternary to Permo-Carboniferous, then warming to Silurian and another cooling to Late Precambrian. The data on which the Mesozoic and Tertiary interpretations were based will be published elsewhere as they are not directly relevant to the subject of this thesis.

The general similarity of the palaeoclimatic and palaeolatitute curves indicates that the palaeomagnetic field for the last 600 m.y. was predominantly of the axial dipole type. The above similarity indicates also that the paleoclimatic zonation was caused in its major part by the same factors as at present day (inclination of the Earth axis, rotation of the Earth and Coriolis forces).

The first order climatic fluctuations were determined by the latitudinal position of the region with respect to the contemporaneous pole position. This is also clear from the correlation of the paleoclimatic curve for the Mesozoic of the Western Carpathians (Veizer, 1970a; Veizer et al., 1971; Veizer and Demovič, in press) with the palaeolatitude data extrapolated from the maps of stable Europe (Briden and Irving, 1964). This extrapolation may be regarded as valid, since the data indicating a shear zone with lateral displacement of alpine Europe by several thousand kilometers (De Boer, 1965;

Irving, 1968) were not confirmed by new measurements. The new data from Dolomites (Manzoni, 1970) confirmed only the differences in declination (rotational movements), but not in inclination.

The second order climatic fluctuations, superimposed on the first order ones, were probably caused by other factors of terrestrial or extra-terrestrial origin (see the review of Schwarzbach, 1963). The most widely believed reasons are fluctuations in the total solar radiation (Öpik, 1950), albedo theory (cf. Emiliani, 1966) or "greenhouse effect" of the CO_2 (Plass, 1956; Dorman, 1968 and others). The aridity and humidity might be also influenced by the contemporaneous continent and relief configuration and other unknown phenomena.

It seems likely that the second order climatic fluctuations were much more pronounced during the periods of glaciation (Quaternary, Permian-Late Carboniferous, Late Precambrian). This might be only an apparent trend due to the easier detection of those fluctuations in geological record. However, judging from the very real climatic fluctuations in Quaternary, I believe the trend is a real one.

There were obviously colder and warmer periods affecting the whole globe as indicated by the simultaneous ice ages on both hemispheres, very widespread global development of red beds in Early Triassic and other simultaneous phenomena. As a result the Mesozoic of Australia was warmer than the Late Carboniferous and Permian, in spite of their similar palaeolatitudes. It seems also that the Paleozoic (except of the Late Carboniferous and Permian) was warmer than the Tertiary, although this may be also attributed to the slight difference in palaeolatitudes or to the differences in relief.

Chapter 3

EVOLUTION OF SEDIMENTARY CARBONATE ROCKS WITH TIME

The evolution in composition of carbonate rocks with time is demonstrated not only by the ratio of limestone/dolomite (Mg/Ca) (see fig. 31), but also by the development of various genetic types within the limestone and dolomite groups.

The total volume of carbonate rocks increases towards younger periods of geological history. Several possible explanations of this trend have been offered in the literature. One of those is the greater abundance of sialic platforms and thus of epicontinental seas in younger geological history (Strakhov, 1969; Ronov, 1964 and others). Another is the ease of erosion and recycling of sedimentary rocks (Garrels and MacKenzie, 1969). According to the latter authors, the half-mass age for carbonates is ~300 m.y. (600 m.y. for shales and 200 m.y. for evaporites) so that the lower volume of carbonates in older sequences could be explained by their destruction. The explanations based on the chemistry of sea water and atmosphere will be discussed later in the text.

In general the oldest sequences (older than 2 b.y.) are composed of algal (biochemical?) limestones and dolomites. The origin of the latter will be discussed later. Sequences between 2 and 1 b.y. old are almost completely early diagenetic (and primary??) dolomites. The proportion of limestones of inorganic and biochemical origin increases in younger sequences. Since the Cambrian, the predominant carbonate sediments are limestones of biological and bioclastic origin and late diagenetic dolomites. The importance of the latter decreases progressively in Mesozoic, Tertiary and Quaternary strata.

The above mineralogical trend is accompanied by gradual spreading of carbonate sedimentary environments from semi-restricted lagoonal and littoral epicontinental environments in the Proterozoic and Cambrian, to neritic shelf (<200 m deep) environments in the Paleozoic, hemipelagic (bathyal, <1000 m) in Triassic and Early Jurassic and finally pelagic (abyssal, >1000 m) environments in Late Jurassic. This trend is a reflection of the simultaneous evolution and migration of carbonate secreting (directly or indirectly) organisms (cf. Strakhov, 1969, p. 293 in the Russian original). Whether the organisms were the direct cause of the carbonate evolution, or whether they only utilised and magnified already established physicochemical conditions remains debateable.

The evolution of carbonates outlined above is basically similar to the trends described by Strakhov (1969), Ronov (1964), Fairbridge (1967a) and others. It differs from them only partly in the timing of changes in the composition and sedimentary environments for Archean and Proterozoic sequences.

Chapter 4

ANALYTICAL TECHNIQUES

The major elements were determined on the Philips 1220 XRF spectrograph at the Department of Geophysics and Geochemistry of the A.N.U.

The linear calibration method for fusion discs of lithium borate and unknown sample was employed, as described by Norrish and Chappell (1967). The matrix correlation of Norrish and Hutton (1969) were used in the computer calculations of the major element composition.

The accuracy of the major element determinations, compared to the recommended values for the AGV-I, BCR-I and GSP-I standards (Flanagan, 1969), was $<1\%$ for TiO_2, Al_2O_3 and total Fe (as Fe_2O_3), $<2\%$ for CaO, SiO_2 and MgO, $<3\%$ for K_2O, $<4\%$ for MnO and $<5\%$ for P_2O_5. The precision of the method expressed as coefficient of variation was $<1\%$ for TiO_2, CaO, K_2O, SiO_2, Al_2O_3, total Fe and MnO, $<3\%$ for MgO and $<5\%$ for P_2O_5.

Rb and Sr were determined on pelletized samples prepared according to the method of Norrish and Chappell (1967). Approximate absolute Rb, Sr values and precise Rb/Sr ratios were measured. These were obtained using X-ray background measurements as a measure of the mass absorption coefficients of Rb and Sr (A_{Rb} and A_{Sr}) (Norrish and Chappell, 1967, method 5, p. 192). Since the ratio A_{Rb}/A_{Sr} varies only slightly with varying sample composition and varies as a function of A_{Rb} or A_{Sr}, precise values for the ratio can be calculated from the approximate absolute values of A_{Rb} and A_{Sr} (Chappell, personal communication, 1971). The equation used was:

$$\frac{A_{Rb}}{A_{Sr}} = \frac{A_{Sr}\ (1.188-0.001643\ A_{Sr})}{Cb_{Quartz} \times 7.1/Bg} \quad ; \quad Bg = Cb - X \times Cf$$

where: Bg = true background, Cb = counted background, x = self tail effect, Cf = peak height - Cb

Thus precise Rb/Sr ratios can be measured. Pb, Th and U were also measured and correction applied for any spectral interference on Rb and Sr (Norrish and Chappell, 1967, p. 187).

The accuracy of the method, compared to the preferred values used by the Department of Geology of the A.N.U. (Chappell, personal communication, 1970), was within 10% for the following standards: W-1 (Rb = 21.44 ppm; Sr = 188.5 ppm), GSP-1 (253.0; 234.5), T-1 (28.6; 373.1), BCR-1 (46.76; 329.4), G-2 (170.0; 482.5), NBS 99a (107.0; 445.7), AGV-1 (67.09; 659.8), NBS 70a (529.9; 65.38). On the average, the measured concentrations were about 7% lower than the preferred values, but the Rb/Sr ratios, which are more relevant to the Sr isotope study, were within 1% limits. The precision of the method expressed as coefficient of variation was $<1.5\%$.

The CO_2 content was calculated from the CaO and MgO determined by the "three aliquot" titration method of Přibil and Veselý (1966). The average difference between the XRF and titration values for CaO and MgO was +4 and +12% respectively. This was partly due to the inhomogeneity of samples, and the difference in the MgO values might be assigned mainly to the low accuracy of both methods (particularly of the XRF) at low MgO concentrations ($<1\%$). The average difference for samples with MgO concentrations $>1\%$ was only +6%.

The samples for FeO determinations were treated with HF + H_2SO_4 in digestion apparatus under N_2 atmosphere and then titrated by constant potentiometry with dichromate solution (Kiss, 1967). The Fe_2O_3 was calculated as a difference between the above Fe^{2+} and total Fe determined by XRF. The accuracy of the FeO determination, compared to the recommended values for

the W-1, BCR-1, T-1, G-2, AGV-1 and GSP-1 (Flanagan, 1969) was better than 3% (Kiss, personal communication, 1970) and the precision expressed as coefficient of variation was $<0.5\%$. Precision on my samples was better than 1.5%, which is about 3 times less than the precision obtained on igneous silicates. This discrepancy might have been caused by the presence of organic matter. Nevertheless, the voltametric end-point detection technique gave reliable data in spite of the unfavorable rock composition for the titrimetric Fe determination.

Determination of Na was made on powdered samples of 0.5-1.0 g size. The procedure utilized was based on simultaneous determination of Na + K with Li internal standard as described by Cooper (1963) for K determinations, however the sodium buffer was not used.

Unknown samples were treated with 6 mls of H_2SO_4 and 40 mls of HF, left overnight, evaporated on the water bath, fumed on hot plate and dissolved in distilled water on the water bath. Afterwards the samples were washed into 250 mls measuring flasks containing 50 mls of 4000 Li internal standard solution and diluted to the 250 mls volume and finally stored in polyethylene bottles.

The measurements were made on a modified model KY3 Baird-Atomic flame photometer using air-propane flame, by bracketing the unknown between the two nearest standards. The majority of samples were between blank and 2 ppm K + Na standard solutions.

The accuracy of the method for Na_2O concentrations above 1% (Kiss, personal communication, 1971) was between 0.6 and 3.1% of recommended values for T-1, NBS-99, G-1 and BCR-1 (Flanagan, 1969; NBS, 1959; Stevens et al., 1960). Precision was within 1%.

The measured concentrations for DTS-1 were 0.016 and 0.012 and for PCC-1, 0.10%. This is within the range of values listed in Flanagan (1969),

but as seen from his table and also from my data the precision and accuracy at such low levels are very poor.

For the isotopic determination of Sr, 0.5 g of sample was dissolved in 0.1 N HCl and an aliquot containing ~20 µg of Sr passed through a cation exchange column to purify the Sr.

The Sr isotopic measurements were made on the Nuclide Analysis Associates 12 inch 60^{o} mass spectrometer in the Department of Geophysics and Geochemistry, using magnetic field switching and the triple filament mode of ionization. The beam intensity for the majority of samples was 10^{-10} amps, and a 2×10^{10} imput resistor was employed. The mean of 21 normalised Sr^{87}/Sr^{86} measurements of the Eimer and Amend standard reported by Arriens and Compston (1968) was 0.70813 with $\sigma_{mean} = 14 \times 10^{-5}$. The mean of an additional 9 measurements made during 1970 (Table 1) was statistically indistinguishable from this.

Table 1: Measurements of the Eimer and Amend standard

Date	Measured by		
February 1970	J. Veizer	.70811	
		.70811	
		.70817	
		.70822	
April 1970	R.W. Page	.70809	
		.70814	
		.70811	
August 1970	J. Veizer	.70815	
		.70813	
	mean	.70814	σ_{mean} 4×10^{-5}

The standard error for 16 duplicate runs (including duplicate disolutions) and 7 duplicate runs of the same samples on different filaments was 23×10^{-5}. Even this value is probably too high, since the repeated samples were mainly those with somewhat higher instability during their original runs.

Chapter 5

AVERAGE CHEMICAL COMPOSITION OF CARBONATE ROCKS

The calculated averages for the whole group of sedimentary carbonate rocks, and for the limestones agree well with published data (Table 2). The discrepancies in FeO and Fe_2O_3 between the present averages and those of Vinogradov and Ronov (in Wedepohl, 1969a) and Wedepohl (1969a), as well as the higher value for MnO in Turekian and Wedepohl (1961) are probably explained by different proportions of the carbonate rocks deposited during humid and arid periods, or by different proportions of dolomites (see Chapters 7 and 8). If these explanations are not sufficient to account for the above discrepancies, the agreement for the total Fe in the first three columns of Table 2 would favour the lower FeO and Fe_2O_3 concentrations. The higher Na_2O content of present samples, compared to the data of Clarke and Turekian and Wedepohl, is probably related to the higher Al_2O_3 content of Australian rocks. The values of 0.14% for MnO and 610 ppm for Sr (Turekian and Wedepohl, 1961) seem to be too high. Graf (1960) reported 475 and Veizer and Demovic (in press) 261 ppm of Sr as an average value. Strontium is obviously variable in sedimentary carbonates but the data support an average value of ~450 ppm. The estimate of the average Rb content by Graf (1960) is very likely too high, although Havard (1967) published 75 ppm as an average Rb content of 130 Devonian silty limestones and Weber (1964) 45 ppm for 120 dolomites.

Table 2. Average chemical composition of sedimentary carbonate rocks

	Carbonate Rocks				Limestones		Dolomites		
	Present data	Clarke (1924)	Turekian and Wedepohl (1961)	Vinogradov and Ronov (1956) in Wedepohl (1969a)	Present data	Wedepohl (1969a)	Present data		
							Σ	early	late diagenetic
No. of Samples	170	345[7]		1500-8300[7]	120	93	50	42	8
%									
SiO_2	7.86	5.19	5.14	8.20	6.81	6.90	10.38	10.64	9.05
TiO_2	0.05	0.06	0.07	-	0.05	0.05	0.05	0.05	0.03
Al_2O_3	1.01	0.81	0.79	2.20	0.98	1.70	1.09	1.14	0.83
Total Fe as Fe_2O_3	0.69	0.54	0.54	-	0.56	-	1.00	1.11	0.40
FeO	0.30[1]	-	-	1.00	0.29[2]	0.98	0.31[3]	0.31	0.35[4]
Fe_2O_3	0.37[1]	-	-	0.68	0.27[2]	1.30	0.59[3]	0.67	0.09[4]
MnO	0.07	0.05	0.14	0.07	0.05	0.08	0.12	0.14	0.04
MgO	6.56	7.90	7.83	7.70	1.71	0.97	18.18	18.11	18.51
CaO	42.45	42.61	42.32	40.50	48.85	47.60	27.09	26.89	28.12
Na_2O	0.11[10]	0.05	0.05	-	0.11[11]	0.08	0.11[12]	0.12[13]	0.05[14]
K_2O	0.37	0.33	0.33	-	0.34	0.57	0.43	0.45	0.31
P_2O_5	0.07	0.04	0.09	0.07	0.08	0.16	0.05	0.06	0.05
ppm									
Sr	425[5]	475±50[6]	610		452[9]	-	122	136	51
Rb	9[8]	70±40[6]	3		8[9]	-	10	10	8

1 - only 155 samples, 2 - only 106 samples, 3 - only 49 samples, 4 - only 7 samples, 5 - excluding 4 Quaternary and Tertiary samples (Σ = 169 samples) with very high Sr concentrations due to the presence of metastable carbonate minerals. If those 4 limestones are included the average content is 548 ppm. 6 - data of Graf (1960), 7 - combined into composite samples and then analysed, 8 - 173 samples, 9 - 123 samples, 10 - 120 samples, 11 - 78 samples, 12 - 42 samples, 13 - 37 samples, 14 - 5 samples.

Chapter 6

THE DISTRIBUTION OF ELEMENTS, ISOTOPES AND THEIR RATIOS

General evaluations of the types of element distribution in limestones and dolomites have been made on the basis of the analysed specimens (120 and 50 samples; 78 and 42 samples for Na_2O).

In general the distribution (judged from histograms, as well as from the tests on probability papers) for both limestones and dolomites seems to be of a lognormal type for total Fe (as Fe_2O_3), MnO, TiO_2, CaO, K_2O, Na_2O, SiO_2, Al_2O_3, Rb and Sr (see figs. 2, 3 and 4). MgO and P_2O_5 are distributed lognormally in limestones. In dolomites MgO shows two lognormal distributions rather than a single normal distribution, and P_2O_5 has a high value tail which is better accommodated in a lognormal than in a normal type of distribution.

Due to the small size of populations (mainly in the case of dolomites), it is difficult to decide whether the types of distribution shown by the histograms represent only one population or several populations with different means. In particular, the Sr, SiO_2, TiO_2, Na_2O and total Fe in limestones, MgO, MnO and total Fe in dolomites might be distributed according to a lognormal law in several populations with different means.

The distribution of CaO in limestones and dolomites and MgO in dolomites have a negative skewness, whereas all the others have a positive one. This negative skewness is due to the scarcity of intermediate carbonate types between the end members (limestone, dolomite, magnesite) in lithified natural rocks (cf. also Fairbridge et al., 1967) and the dilution of these "pure" end members by insoluble residue fraction.

The same general patterns of distributions and their limitations are observed also for the element ratios (e.g. element/carrier), such as the

total Fe/Al_2O_3, SiO_2/Al_2O_3, MnO/total Fe, $(Sr/Ca) \times 10^3$, Fe^{2+}/Fe^{3+} and $(Mg/Ca) \times 10^2$ of limestones and dolomites. The $(Mg/Ca) \times 10^2$ of dolomites and Sr^{87}/Sr^{86} ratios of limestones are distributed normally. The histogram of Sr^{87}/Sr^{86} of dolomites very likely indicates several populations with possibly normal types of distribution.

Figure 2. Histograms of the Al_2O_3, SiO_2, TiO_2, K_2O, Na_2O and Rb distributions.

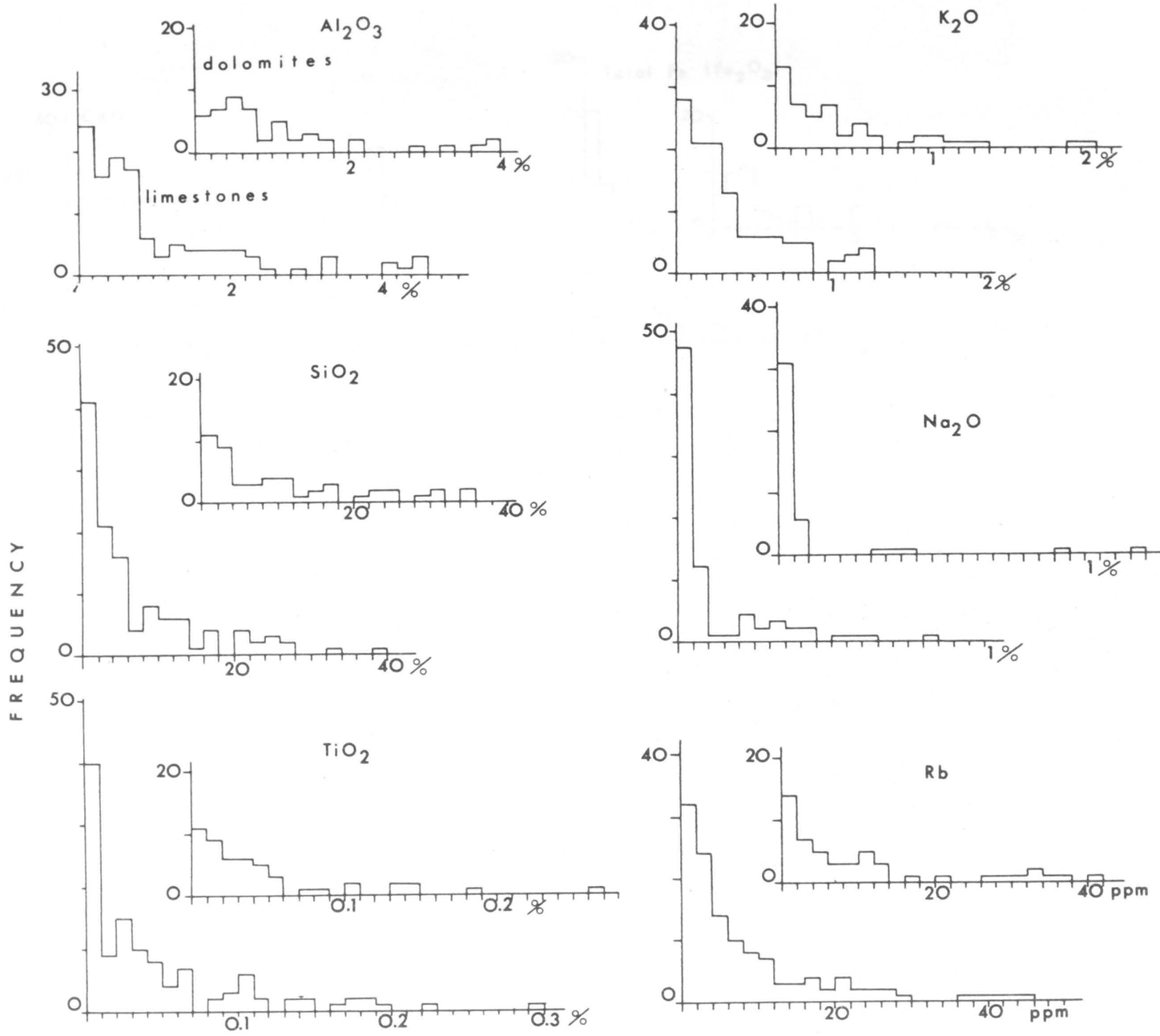


Figure 3. Histograms of the CaO, MgO, Total Fe, MnO, P_2O_5 and Sr distributions.

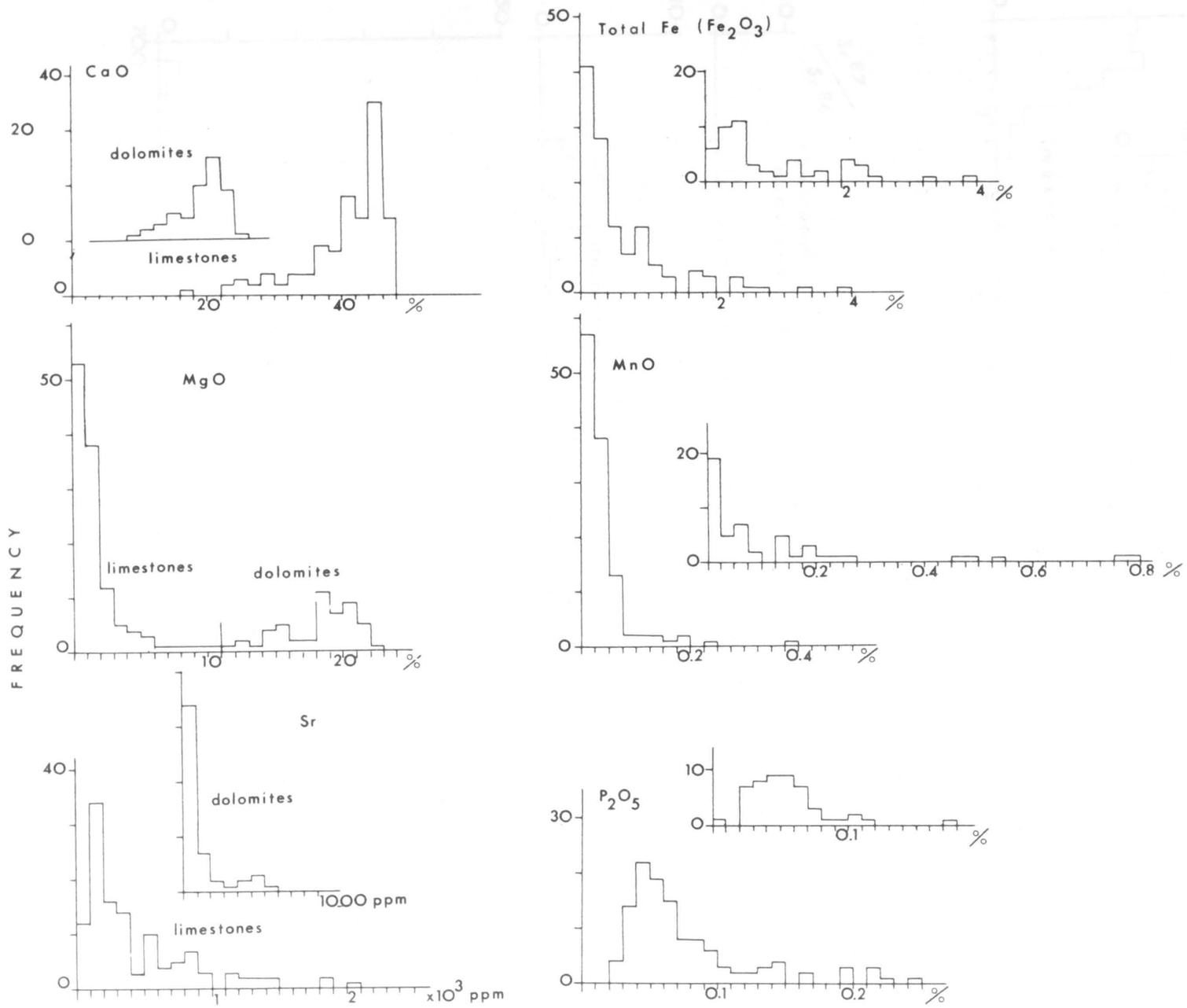
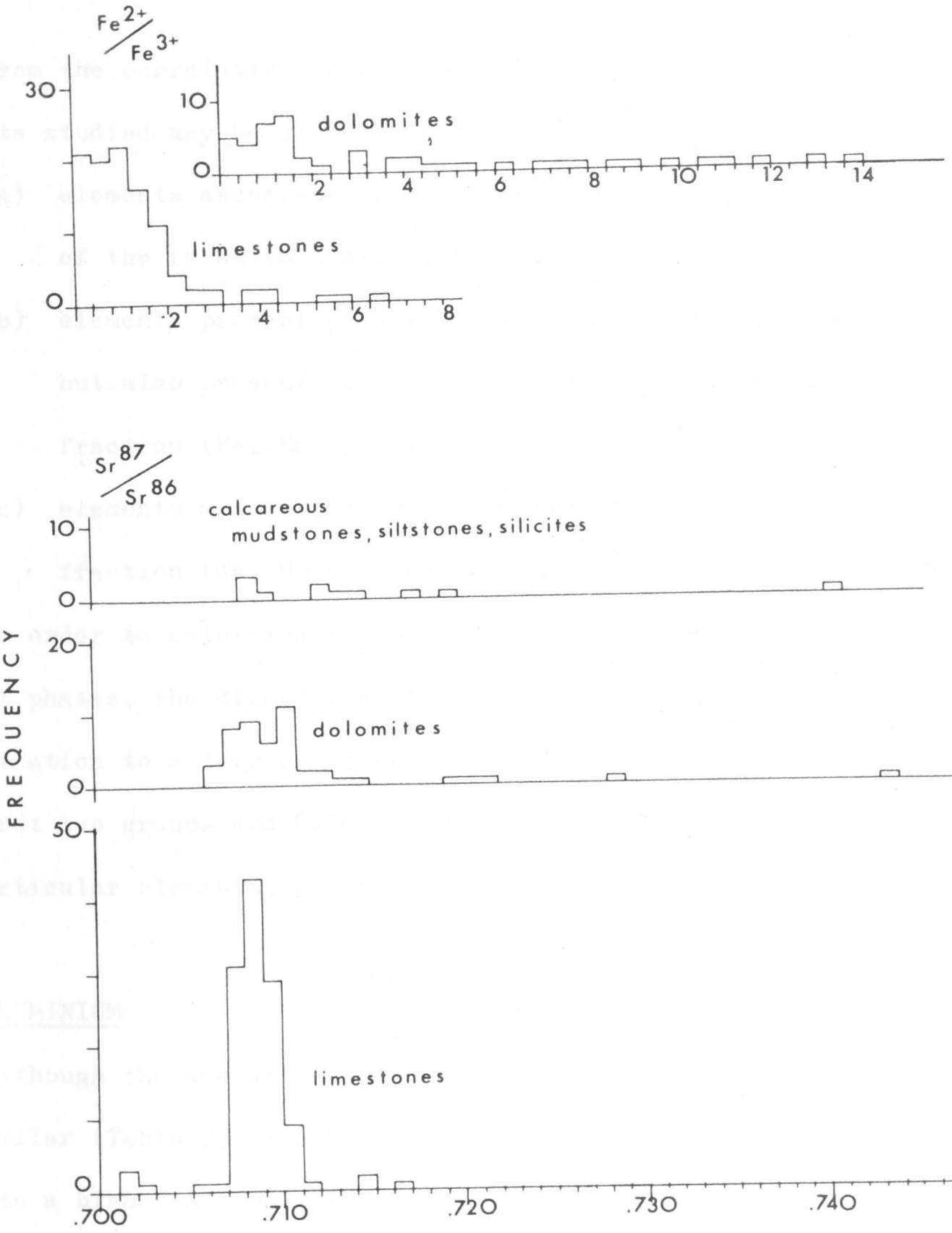


Figure 4. Histograms of the Fe^{++}/Fe^{+++} and Sr^{87}/Sr^{86} distributions.



Chapter 7

FACTORS CONTROLLING ELEMENT DISTRIBUTION

From the correlation coefficients (Table 3) it is obvious, that the elements studied may be divided into three major groups:

(a) elements associated predominantly with the silicate fraction of the rocks (Si, Al, K, Na, Ti and Rb),

(b) elements present predominantly in the silicate fraction, but also present in substantial amounts in the carbonate fraction (Fe, Mn and P),

(c) elements associated predominantly with the carbonate fraction (Ca, Mg and Sr).

In order to determine the proportions of the elements in various mineral phases, the discussion of their distribution is based on their normalization to a carrier phase. These are aluminosilicates (Al_2O_3) for the first two groups and $CaCO_3$ (CaO) for Sr. The chronological discussion for particular elements, except of Sr, is presented in this chapter.

7.1 ALUMINIUM

Although the average Al_2O_3 concentrations for limestones and dolomites are similar (Table 2), the histograms of its distributions (fig. 2) indicate a higher Al content for dolomites. The mode for limestones is between 0-0.4% and for dolomites between 0.4-0.8%. The positive correlation of the dolomite content with insoluble residue in carbonate sequences was observed by several previous authors (cf. Fairbridge et al., 1967). This was attributed to the more intimate association of dolomites with shorelines, compared to limestones. Other authors (cf. Veizer, 1970a) argued, that the fine-grained aluminosilicate phase might play an important role

Table 3. Linear correlation coefficients of elements in sedimentary carbonate rocks
n = 170 (120 for Na_2O)

	Total Fe	MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	Rb	Sr	Sr^{87}/Sr^{86}	Sr/Ca	Mg/Ca	Si/Al	Tot. Fe/Al	Mn/Al	Mn/Tot. Fe
MnO	0.437																		
TiO_2	0.604	-																	
CaO	-0.474	-0.190	-0.269																
K_2O	0.585	0.234	0.604	-0.376															
P_2O_5	0.235	-	0.349	-	0.159														
SiO_2	0.425	-	0.487	-0.586	0.575	-													
Al_2O_3	0.638	-	0.819	-0.362	0.817	0.232	0.612												
MgO	0.249	-	-	-0.861	-	-0.213	-	-											
Na_2O	0.357	-	0.672	-0.210	0.334	-	0.356	0.686	-										
Rb	0.565	-	0.702	-0.367	0.884	0.163	0.601	0.943	-	0.550									
Sr	-	-	-	0.196	-	-	-	-	-0.303	0.300	-								
Sr^{87}/Sr^{86}	0.407	0.337	-	-0.374	0.422	-	0.281	0.220	0.258	-	0.266	-							
Sr/Ca	-	-	-	-	-	-	0.168	-	-0.207	0.403	-	0.964	-						
Mg/Ca	0.285	0.152	-	-0.902	-	-0.209	0.217	-	0.983	-	-	-0.292	0.314	-0.187					
Si/Al	-	-	-	-0.301	-	-	0.436	-0.156	-	-	-	-	-	-	0.192				
Tot. Fe/Al	0.317	0.193	-	-0.169	-	-	-	-	0.247	-	-	-	-	-	0.224	0.363			
Mn/Al	0.243	0.503	-	-	-	-	-	-0.176	0.182	-	0.170	-	-	-	0.162	0.449	0.808		
Mn/Tot. Fe	-	0.710	-	-	-	-	-	-	-	-	-	-	-	-	-	0.197	-	0.493	
Fe^{2+}/Fe^{3+}	0.270	0.184	-	-0.394	-	-	-	-	0.468	-	-	-	0.214	-	0.441	-	0.372	0.337	-

Dash means that the linear correlation coefficient is not statistically significant at the 95% confidence level.

in the formation of some types of early diagenetic dolomites. On closer examination of data (fig. 2), it seems that the Al distribution in limestones is dominated by two populations; a sharper population with the mode of ~0.1% of Al_2O_3 and a broader one with the mode of ~0.5-0.6%. The latter is very similar to the dolomite population. The "0.1%" population could be identified with organogenic and organodetrital (reef-like) rocks.

At this stage it is not possible to conclude, with certainty, if the early diagenetic dolomites contain higher Al_2O_3 concentrations, compared to the other carbonate types, as suggested by Veizer (1970a).

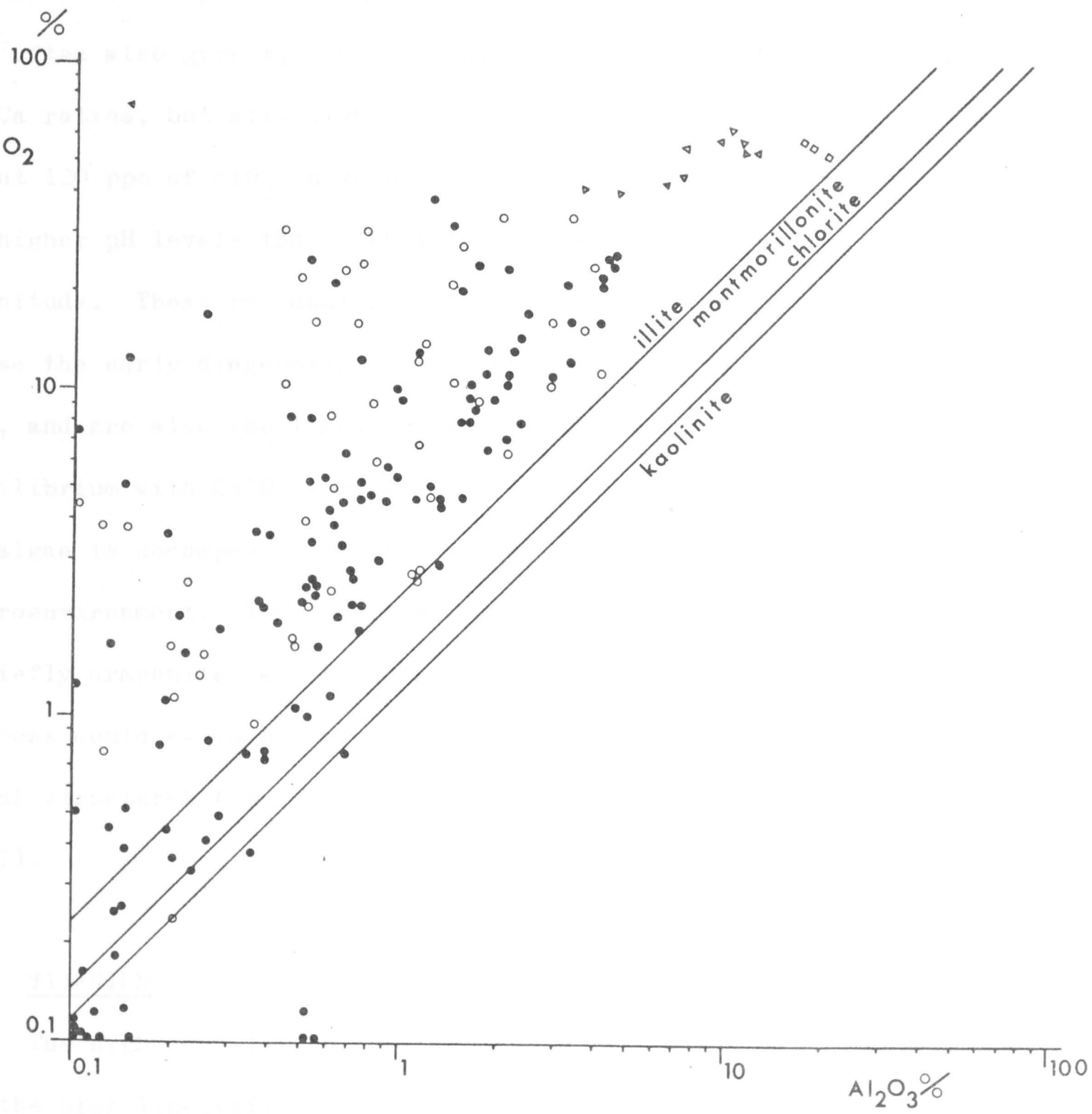
7.2 SILICA

From Table 2 it is evident, that the average SiO_2 content of dolomites is almost 4% higher than of limestones. The higher positive skewness for dolomite population was indeed observed on the SiO_2 distribution histograms (fig. 2). As described previously, the SiO_2/Al_2O_3 ratio of the rocks is of greater importance than the SiO_2 content.

The SiO_2-Al_2O_3 scatter diagram (fig. 5) shows quite clearly that majority of samples have SiO_2/Al_2O_3 ratios above the field of "average" clay minerals calculated from the data of Deer et al. (1964a,b).

The regression is close to the SiO_2/Al_2O_3 ratio of 6:1. This type of scatter indicates presence of free SiO_2, either as quartz or chalcedony. Microscopic studies of thin sections, revealed difference between the mineralogical mode of SiO_2 in limestones and early diagenetic dolomites (which constitute 84% of all studied dolomites). Whereas in limestones the SiO_2 is present mainly as detrital quartz, in dolomites the prevailing phase is chalcedony. The chalcedony was observed in 46% of dolomitic thin-sections and only in 4% of limestone thin-sections (half of the latter

Figure 5. Scatter diagram of SiO_2 vs. Al_2O_3.
Explanations:
full circles - limestones, empty circles - dolomites, squares - mudstones, full triangles - silicites, empty triangles - siltstones.



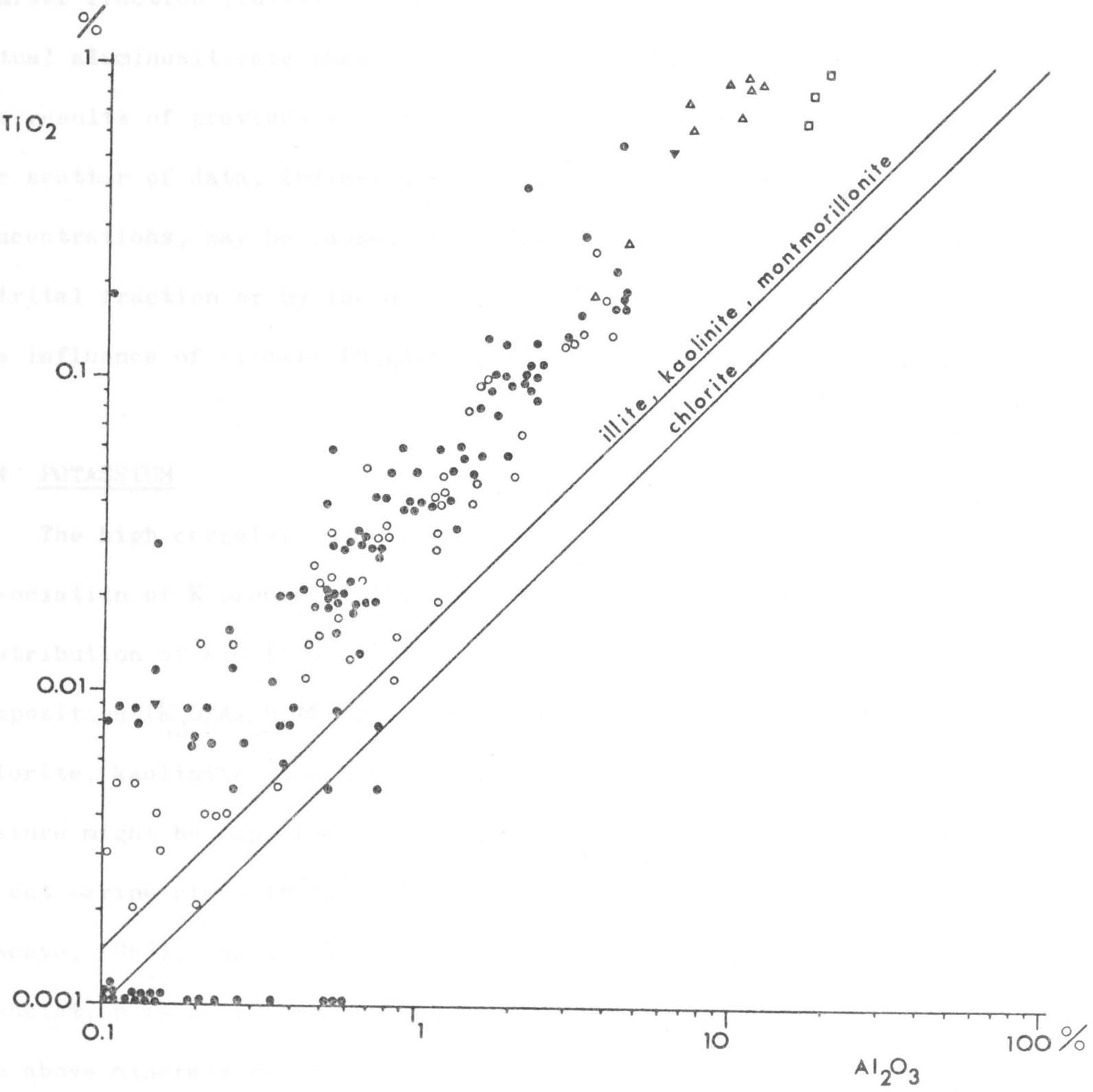
were associated with the early diagenetic dolomites). The chalcedony is very common in algal structures throughout the whole Proterozoic era.

This difference was very likely caused by differences in Eh-pH conditions of their respective sedimentary environments. The early diagenetic dolomites are generally sediments of semi-barred "hypersaline" environment (cf. Friedman and Sanders, 1967; Veizer, 1970a and others). This observation is supported also by lithological analysis of sequences presented in chapters 2 and 3. After initial precipitation of aragonite and often also gypsum, the residual solutions have not only very high Mg/Ca ratios, but also high pH. The solubility of amorphous silica gel is about 120 ppm of SiO_2 in solutions with pH$\leq$9 (Krauskopf, 1967 p. 168). At higher pH levels the solubility increases sharply by an order of magnitude. These residual solutions, after being trapped into sediments, cause the early diagenetic dolomitization of the unconsolidated carbonate mud, and are also the likely source of silica (pH$\sim$9.8 at 25^{o}C and in equilibrium with $CaCO_3$ - Siever, 1957). After burial the organic matter of algae is decomposed and this lowers the pH of the surrounding microenvironment. The lower pH initiates solution of the original carbonate (chiefly aragonite) and simultaneous coagulation of the silica gel. This process could explain the concentrations of chalcedony in and around algal structures (cf. similar examples by Fairbridge, 1967b and Dapples, 1967).

7.3 TITANIUM

The high correlation coefficient of TiO_2 and Al_2O_3 (+0.819) as well as the high linearity of the regression of these two oxides on a log-log scale (fig. 6) indicate unquestionably the presence of Ti in the non-carbonate fraction (cf. Graf, 1960; Migdisov, 1960; Goldberg and Arrhenius, 1958

Figure 6. Scatter diagram of TiO_2 vs. Al_2O_3.
Explanations as in figure 5.

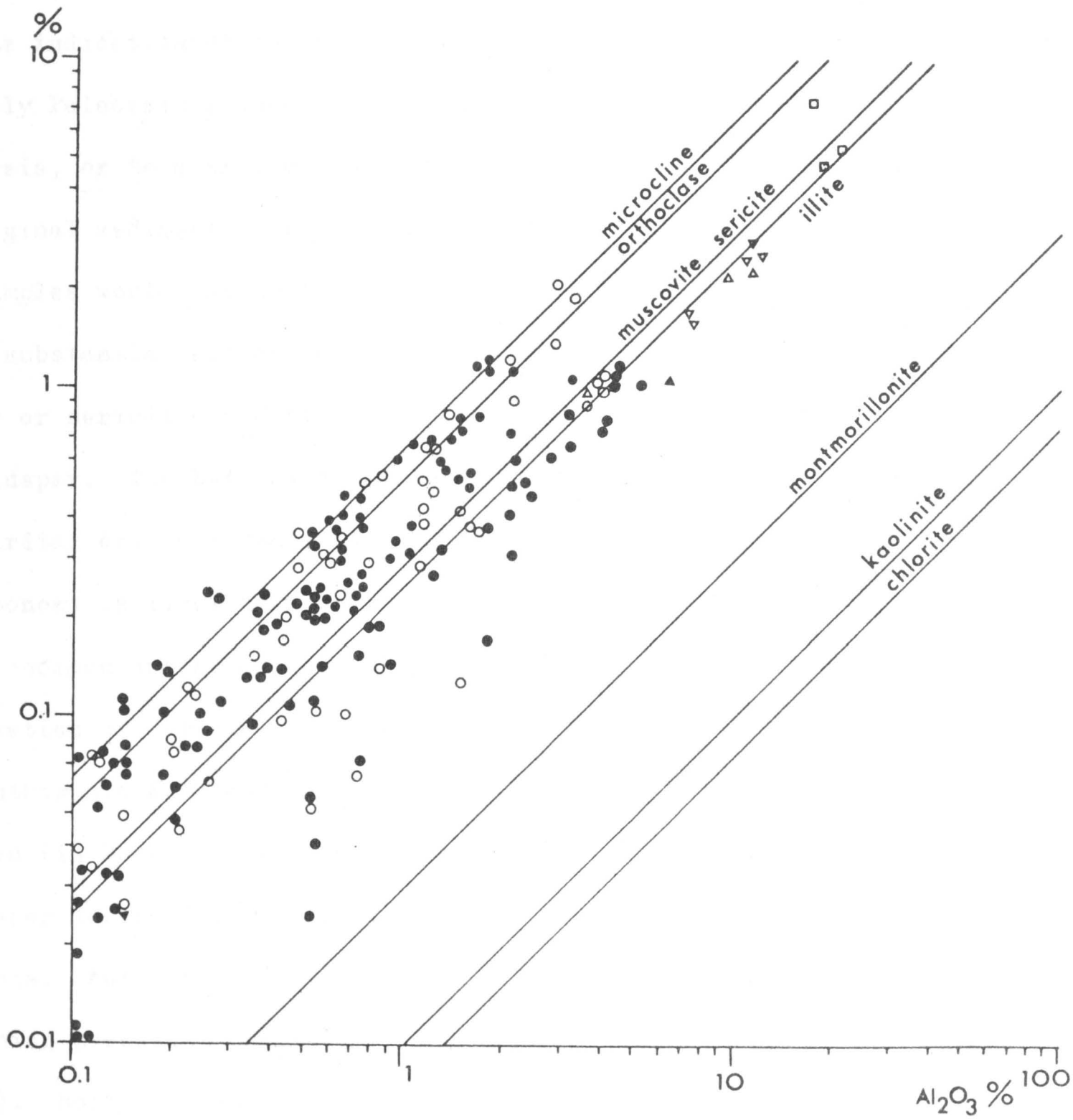


and Veizer and Demovic, in press). The regression is close to the TiO_2/Al_2O_3 ratio of 0.05, which is similar to the average ratio of the Russian Platform mudstones (Migdisov, 1960). However, the majority of TiO_2 values are above the field of "average" clay minerals. The highest Ti/Al ratios were observed in siltstones. This would point to the Ti concentration in a coarser fraction (rutile, ilmenite, brookite and anatase) and not in the actual aluminosilicate phase. The above explanation is consistent with the results of previous authors (Graf, 1960; Migdisov, 1960 and others). The scatter of data, indicated by the presence of the few higher Ti concentrations, may be caused by different proportion of the coarser detrital fraction or by the differences in the parent source rock material. The influence of climate (Migdisov, 1960) was in this case negligible.

7.4 POTASSIUM

The high correlation coefficient (+0.817) of K_2O/Al_2O_3 indicates association of K predominantly with the aluminosilicate phase. The distribution of K_2O (fig. 7) in general follows the "average" illite composition ($K_2O/Al_2O_3 \approx 0.25$). The data also indicate low abundance of chlorite, kaolinite, montmorillonite and mixed layer clay minerals. This feature might be expected, since illite generally constitutes 60-80% of recent marine clays (Müller, in Füchtbauer and Müller, 1971, p. 161; Biscaye, 1965), and according to Millot (1949) the kaolinite-limestone association is an incompatible one. Nevertheless the virtual absence of the above minerals would demand influences of some other factors as well. The most likely explanation might be the age of the rocks. Since the kaolinite-montmorillonite assemblage is converted to illite-chlorite (Müller, 1967; Weaver, 1967; Keller, 1970; Kossowskaya, 1971 and others) at temperatures $\sim 150^{\circ}C$ and >1.2 kb burial pressure, it is unlikely that

Figure 7. Scatter diagram of K_2O vs. Al_2O_3.
Explanations as in figure 5.



the "metastable" assemblage would be preserved in substantial quantities in rocks older than Mesozoic. In the Mesozoic carbonate sequences of the West Carpathians the predominant clay mineral is illite. Chlorite is less common and kaolinite and montmorillonite are detected only sporadically (Veizer, 1968b). The presence of the last three minerals fluctuated according to the climatic conditions on the adjoining land areas.

The indication of the small proportion of chlorite in the Precambrian and Early Paleozoic sequences possibly points to a low degree of deep burial diagenesis, or to a predominantly monomineralic (illitic) composition of the original sediment. Presence of macroscopically visible sericite in some samples would favour the second assumption.

A substantial proportion of the samples falls outside the range of illitic or sericitic K_2O/Al_2O_3 ratios. They seem to fit the composition of a K-feldspar. The K-feldspar could be of detrital or authigenic origin. The detrital origin is unlikely, since the K content of the coarser fraction (siltstones) is lower than of the mudstones. The generally peneplained relief, common during deposition of carbonates, also would not favour preservation of detrital feldspars.

Authigenic K-feldspars are common in sedimentary rocks of all types. Straaten (in Deer et al., 1964b) and Swett (1968) advocated growth of K-feldspar during dolomitization and recrystallization of carbonate sediments. Authigenic K-feldspar is also very common in sediments containing pyroclastic material (Müller, in Füchtbauer and Müller, 1970 p. 231). Both explanations would be compatible with the above data and both might have been active. Somewhat better correlation of high K/Al ratios with the presence of volcanics than with the dolomite content and recrystallization would favour the second alternative. In the McArthur Group (van den Heuvel, 1969; M.C. Brown, personal communication, 1970)

the beds with high K-feldspar content were identified with a high degree of certainty as original tuffs.

7.5 SODIUM

The high correlation coefficient (+0.686) of Na_2O with Al_2O_3 indicates its association with aluminosilicates. Scatter diagram of Na_2O vs. Al_2O_3 (fig. 8) favours illite and (authigenic) orthoclase as the most important mineralogical host phases. This confirms the conclusion advocated on the basis of K_2O/Al_2O_3 data.

7.6 K_2O/Na_2O

The distribution of data as indicated in fig. 9 would again be consistent with illite + authigenic orthoclase as the most important host phases. The clusters of values below orthoclase ratios indicate presence of plagioclases, of probable authigenic origin rather than of kaolinite, montmorillonite and chlorite. This conclusion may be supported by two observations:

(a) samples with high K_2O/Na_2O ratios are characterised also by high K_2O/Al_2O_3 as well as Na_2O/Al_2O_3 ratios. Their Na_2O/Al_2O_3 values are above the fields of kaolinite, montmorillonite and chlorite. This would indicate simultaneous presence of K-feldspars and plagioclases, both very likely of authigenic origin.

(b) the age of the samples is more than 340 m.y. (older than Carboniferous) and, as discussed in the K section, kaolinite and montmorillonite are very rare in sequences of this age. The presence of higher concentrations of chlorite may be excluded on the basis of K_2O/Al_2O_3 data.

Figure 8. Scatter diagram of Na_2O vs. Al_2O_3.
Explanations as in figure 5.

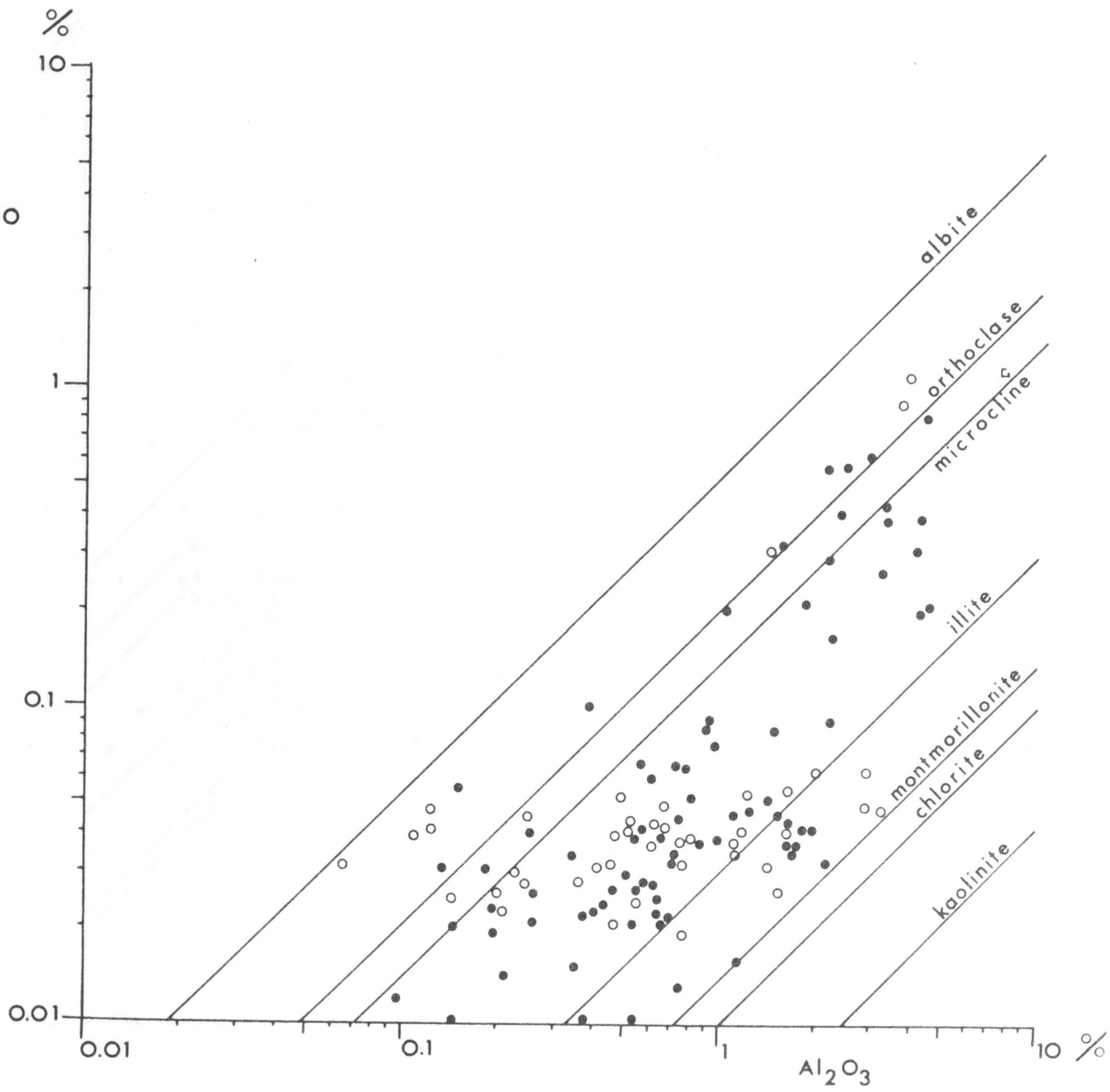
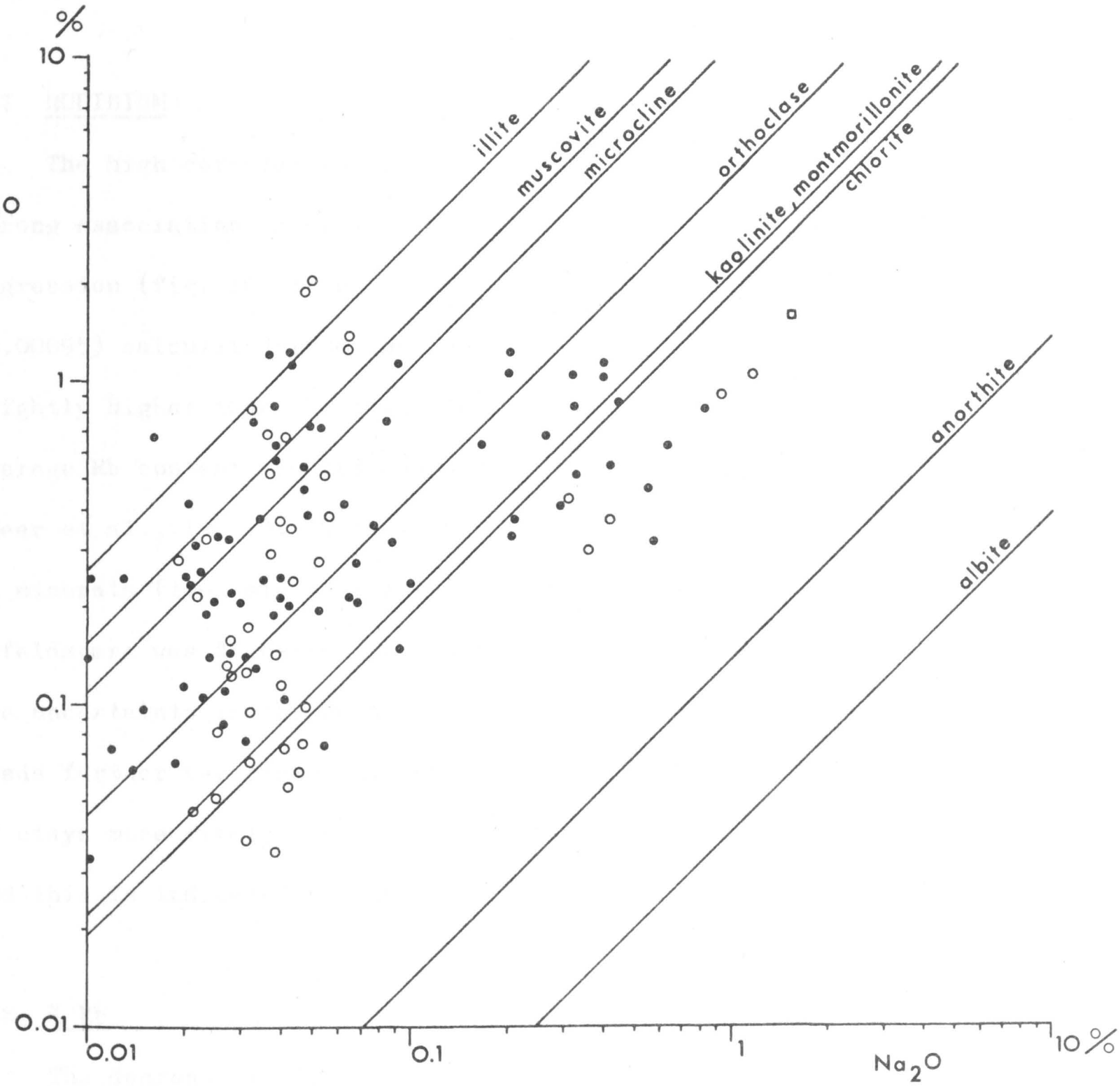


Figure 9. Scatter diagram of K_2O vs. Na_2O.
Explanations as in figure 5.



At the present stage it is difficult to decide whether the alkalies were present in the system since its deposition, and were thus inherited from the source rocks, or were introduced during its diagenetic history. This problem alone would require separate study and is above the scope of this thesis. It is probable however, that at least parts of the alkalies present in the rocks were inherited from the source material.

7.7 RUBIDIUM

The high correlation of Rb with Al_2O_3 and K_2O (Table 3) indicates strong association of Rb with illite (cf. also Horstman, 1957). The regression (fig. 10) is close to the average Rb/Al_2O_3 value for shales (0.00095) calculated from the data of Turekian and Wedepohl (1961) and slightly higher than the value for pure illites (0.00063) calculated from average Rb content 190 ppm (Horstman, 1957) and average Al_2O_3 content 30% (Deer et al., 1964a). This might indicate the presence of some other high Rb minerals (i.e. micas or K-feldspars). The presence of authigenic K-feldspars was discussed in the previous paragraph, however in view of the uncertainty in the Rb/Al_2O_3 estimate of the illite this conclusion needs further verification. Rb in general is held in absorption positions of clays more firmly than K (Horstman, 1957; Heier and Billings, 1970), and this is indicated also by their correlation coefficients (Table 3).

7.8 K/Rb

The decrease in linear correlation coefficients between K, Rb and Al in the order Rb/Al (0.943) > Rb/K (0.884) > K/Al (0.817) and thus the higher retention of Rb in aluminosilicates might explain the generally low K/Rb ratios (~150) of shales, found by previous authors (Horstman, 1957; Heier and Adams, 1964; Heier and Billings, 1970). In the present case, however,

Figure 10. Scatter diagram of Rb vs. Al_2O_3. Explanations as in figure 5.

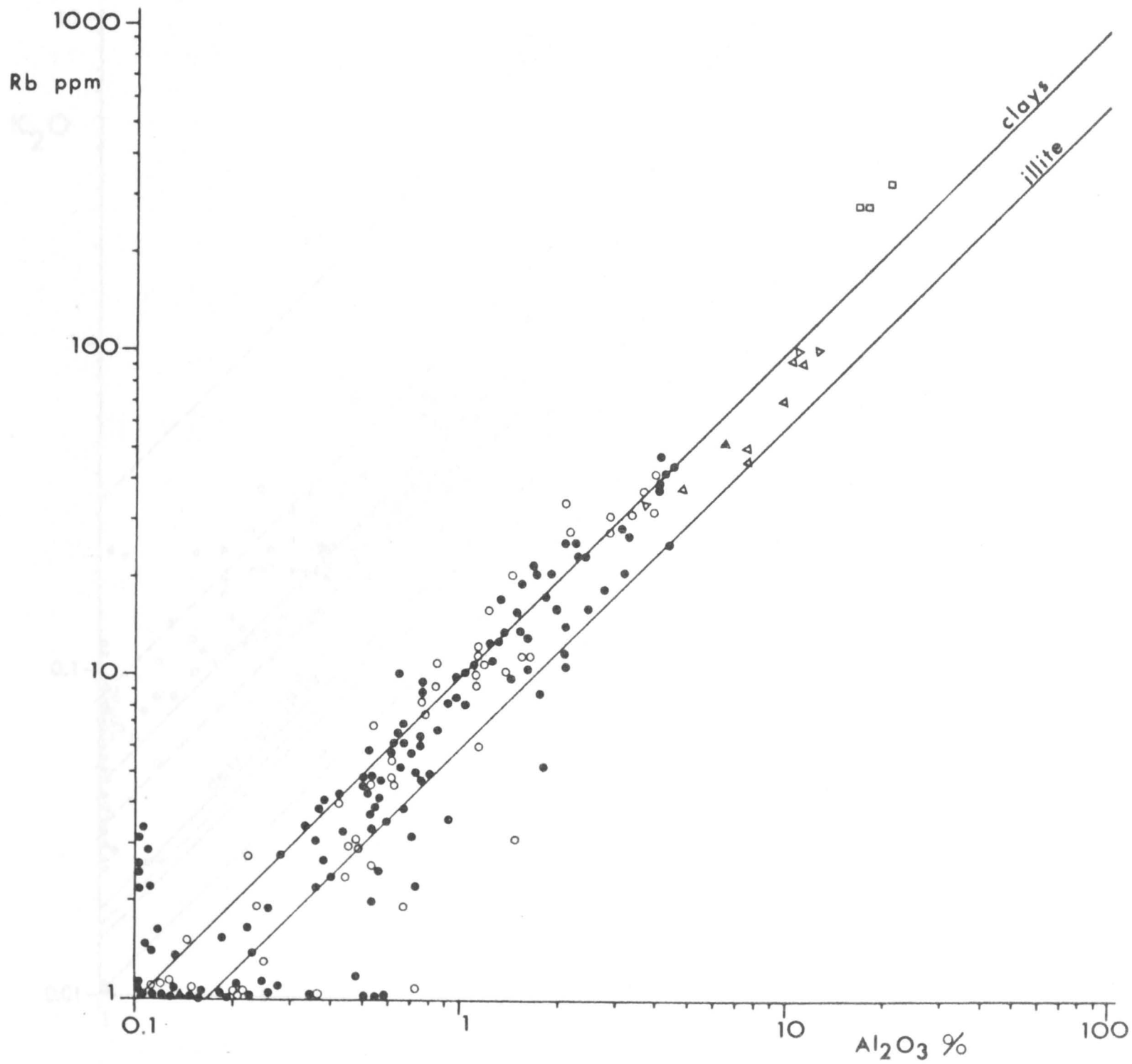
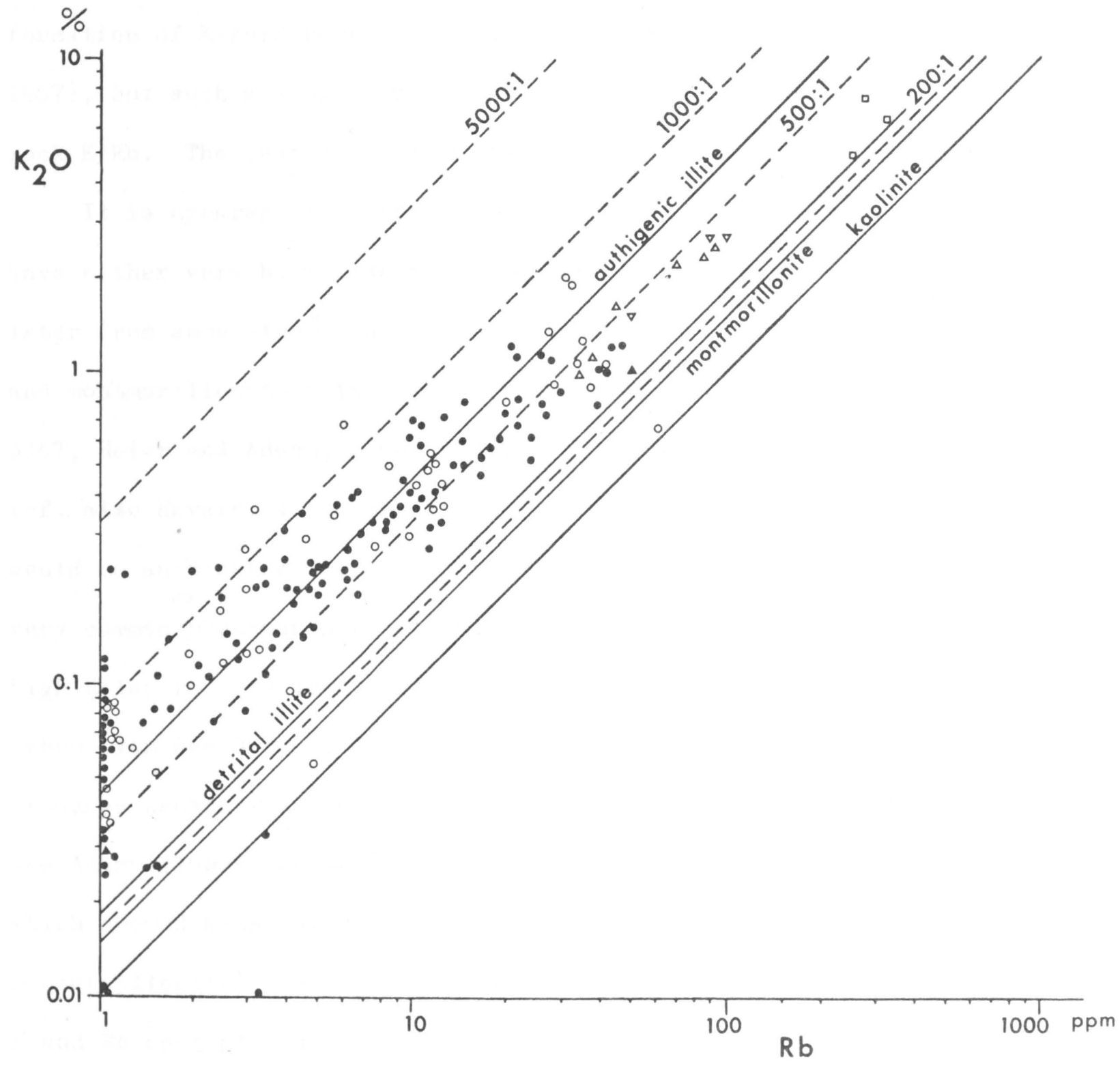


Figure 11. Scatter diagram of K_2O vs. Rb.
Explanations as in figure 5. The ratios marked in the scatter diagram are for K vs. Rb.



the substantial majority of samples have K/Rb ratios above the field of clay minerals (fig. 11). Presence of igneous plagioclase (K/Rb$\sim$500, Heier and Billings, 1970) would be difficult to reconcile with the high K content. Igneous K-feldspar (K/Rb$\sim$200) or detrital illite (K/Rb$\sim$240, Schroll, 1968) would not satisfy the required K/Rb ratios. Authigenic illites (K/Rb$\sim$500, Schroll, 1968) and authigenic K-feldspars (K/Rb$>$500, Reynolds, 1963) could satisfy both, the K/Al and K/Rb ratios. Authigenic formation of K-feldspars from illites is also known to exclude Rb (Horstman, 1957), but such a simple transformation probably would not change the whole rock K/Rb. The last assumption would again require high original K/Rb ratio.

It is apparent from this discussion that the initial material should have either very high K/Rb ratio or low Rb content with K being introduced later from some other source. Authigenic growth of illite from kaolinite and montmorillonite with absorption of K from trapped sea water (K/Rb = 3167, Heier and Adams, 1964) or pore waters might be one possible process (cf. also Havard, 1967, in Heier and Billings, 1970). Another possibility would be authigenic formation of K-feldspars from volcanic tuffs. This is very common phenomenon as already discussed in the previous section. The high K layers were identified as original tuffs at least for the McArthur Group (van den Heuvel, 1969). Alteration of mafic igneous eruptive rocks produces bentonites (Deer et al., 1964a, p. 240). In the data of Heier and Adams (1964) bentonites were also the only group of argillaceous rocks which showed K/Rb ratios above 230. Formation of bentonites (mainly montmorillonite) from volcanics with high K/Rb ratios (300- 1000) and low K and Rb content and their later diagenetic transformation into K-feldspar and illite? by alteration with trapped waters might be satisfactory explanation of the high K/Rb as well as K/Al values. Whether the process included an intermediate stage with formation of zeolites (i.e. analcime)

or leucite (van den Heuvel, 1969; Hay, 1966) or proceeded directly, is difficult to judge, but the presence of high Na together with high K layers in the Carpentarian sequence of Mt. Isa (van den Heuvel, 1969) would favour the zeolite explanation. The basic argument however would not be affected by any alternative.

The decrease of K/Rb with increasing K (fig. 11) has very likely an age significance and will be discussed in Chapter 8. Leash (1967, in Heier and Billings, 1970) observed higher K/Rb for Precambrian argillites (~270) compared to younger shales (~150). He suggested that this was caused by a continuous recycling of clays. From the description in Heier and Billings the exact meaning of this explanation is not clear. Two possible alternatives are that with increasing degree of recycling in younger periods the loss of K has been higher than the loss of Rb due to its lower retention in clays, or that the proportion of recycled detrital illite in argillites has been increasing towards younger ages. The second alternative seems to be of greater importance, but both might have been active.

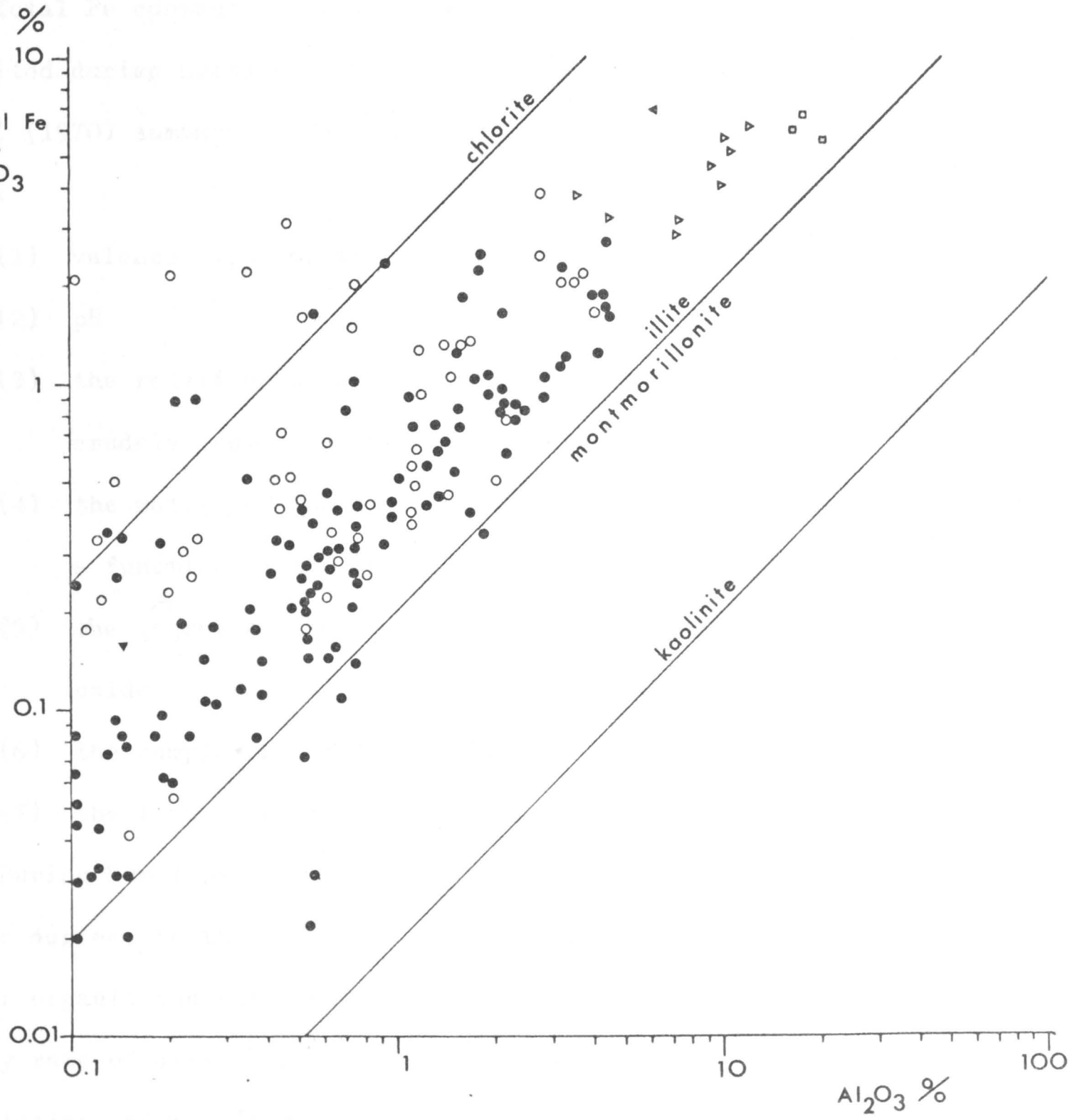
7.9 IRON

The highest correlation of total Fe (as Fe_2O_3) is observed with Al_2O_3 (0.638). This would indicate either its presence in clays, or its association with the clays as a detrital constituent (Fe oxides).

From fig. 12 it is evident, that the Fe_2O_3 values are in excess of those expected for clay minerals (chlorite may be excluded on the basis of K data). This would indicate its presence in the form of Fe oxides and/or Fe carbonates.

The average total Fe content of dolomites is twice that of limestones (Table 2). This conclusion is supported also by the Fe/Mg and Fe/Ca correlation coefficients (Table 3) and the histograms of Fe distribution

Figure 12. Scatter diagram of total Fe vs. Al_2O_3. Explanations as in figure 5.



(fig. 3). The high Fe content is very likely only a feature of early diagenetic dolomites. The difference cannot be attributed entirely to the age factor (Chapter 8), since the higher Fe content of early diagenetic dolomites is observed even in contemporaneous rocks. This difference might be explained by similar ionic radii of Mg^{++}, Fe^{++} and Mn^{++} as compared to the larger Ca^{++}, and by the ease of Fe^{++} substitution for Mg^{++} in the dolomite type of structure (Graf, 1960).

Total Fe content of post-Cambrian limestones is higher for rocks deposited during humid periods than during arid periods (fig. 13). Ghose et al. (1970) summarised factors affecting solubility of Fe in the following order:

(1) valence state of iron in the solids

(2) pH

(3) the relative oxidation state of the aqueous system which is crudely indicated by measured pH

(4) the nature of the solid iron phases present which are in turn a function of the concentration of H_2S, CO_2 etc.

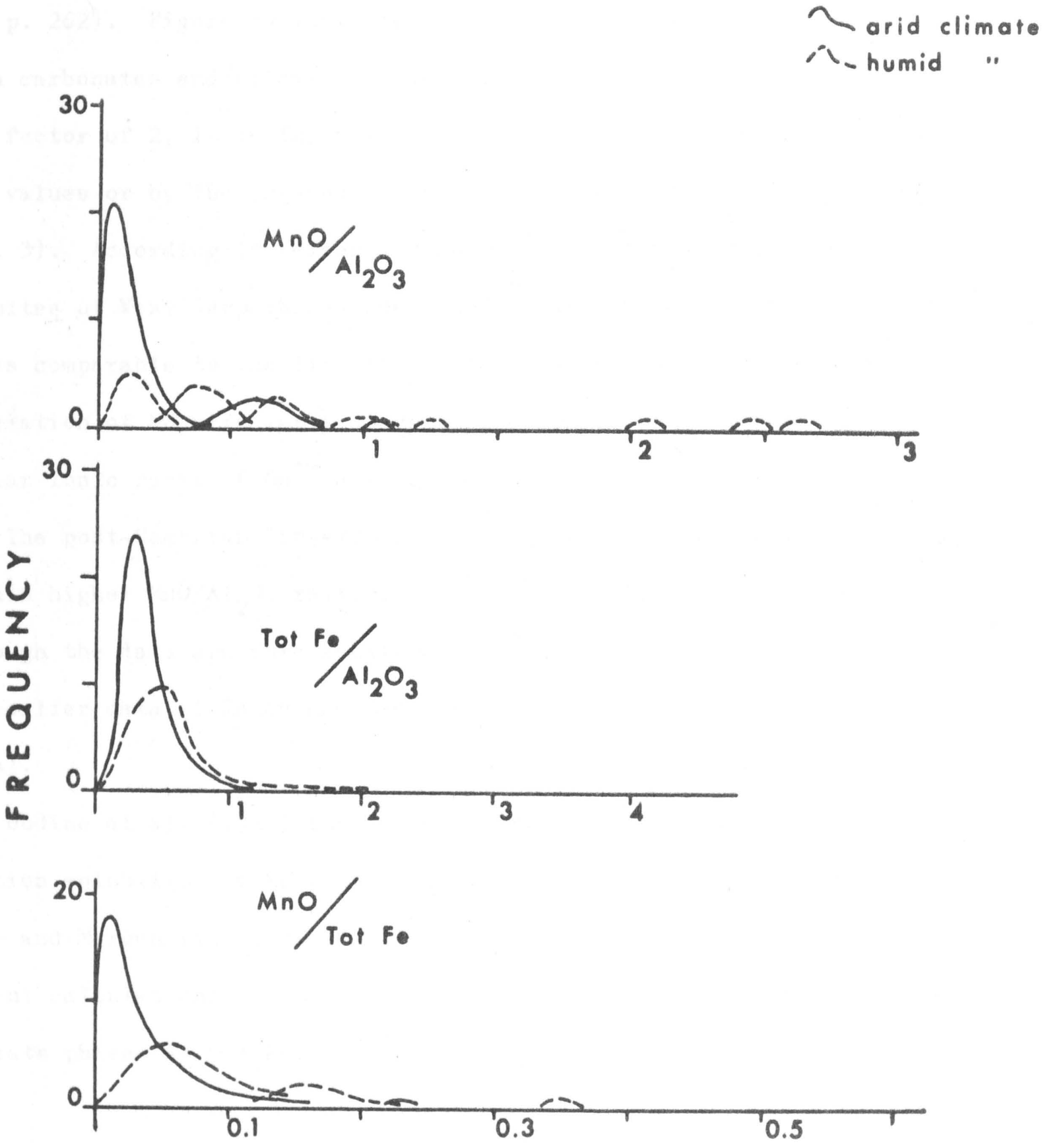
(5) the degree of hydration and crystal form of hydrated ferric oxide

(6) the complexing of ferric iron by inorganic anions

(7) the formation of organic chelates

During humid periods all these factors are shifted, to a greater or lesser degree, in the direction of higher solubility (more water and higher organic content, lower pH and Eh, etc.). This leads to a higher supply rate of dissolved, colloidal and suspended Fe and its precipitation, coagulation and settling upon entering the marginal basins of the sea (cf. also Krauskopf, 1967 p. 259; Borchert, 1960 and others). The association of almost all Phanerozoic economic Fe deposits with humid periods and

Figure 13. Histograms of MnO/Al_2O_3, Total Fe/Al_2O_3 and $MnO/Total\ Fe$ ratios for arid and humid post-Cambrian periods.



humid climatic belts (Strakhov, 1967) supports this conclusion.

7.10 MANGANESE

The chemistry of Mn resembles that of Fe very closely (Krauskopf, 1967 p. 262). Figure 14 indicates, as in the case of Fe, presence of Mn in Mn carbonates and/or oxides. The higher average Mn content of dolomites, by a factor of 2, is in this case caused probably by several anomalously high values or by the presence of several Mn populations in dolomites (fig. 3). According to Veizer and Demovic (in press) early diagenetic dolomites of West Carpathians contained Mn/Ti (and consequently also Mn/Al) values comparable to the limestones of humid periods. The preferential association of Mn with early diagenetic dolomites was attributed to the similar ionic radii of Mn^{++} and Mg^{++}.

The post-Cambrian limestones of humid periods also in this case contain higher MnO/Al_2O_3 ratios, compared to their arid counterparts, although the data are more scattered than for Fe (fig. 13). This corroborates the earlier data of Ronov and Ermiskhina (1959) and Veizer and Demovic (in press).

Bodine et al. (1965) published distribution coefficient for solid solution solubility of $MnCO_3$ in calcite. The problem is also discussed by Stumm and Morgan (1970, p. 207). The data are however of little use in present calculations, since the distribution of Mn between carbonate and silicate phases is not known.

7.11 MnO/TOTAL Fe (Fe_2O_3)

In view of the similarity in chemical behaviour of Mn and Fe, it is important to search for possible discrepancies in their ratios. The scatter diagram (fig. 15) indicates wide spread in Mn/Fe data, although

Figure 14. Scatter diagram of MnO vs. Al_2O_3.
Explanations as in figure 5.

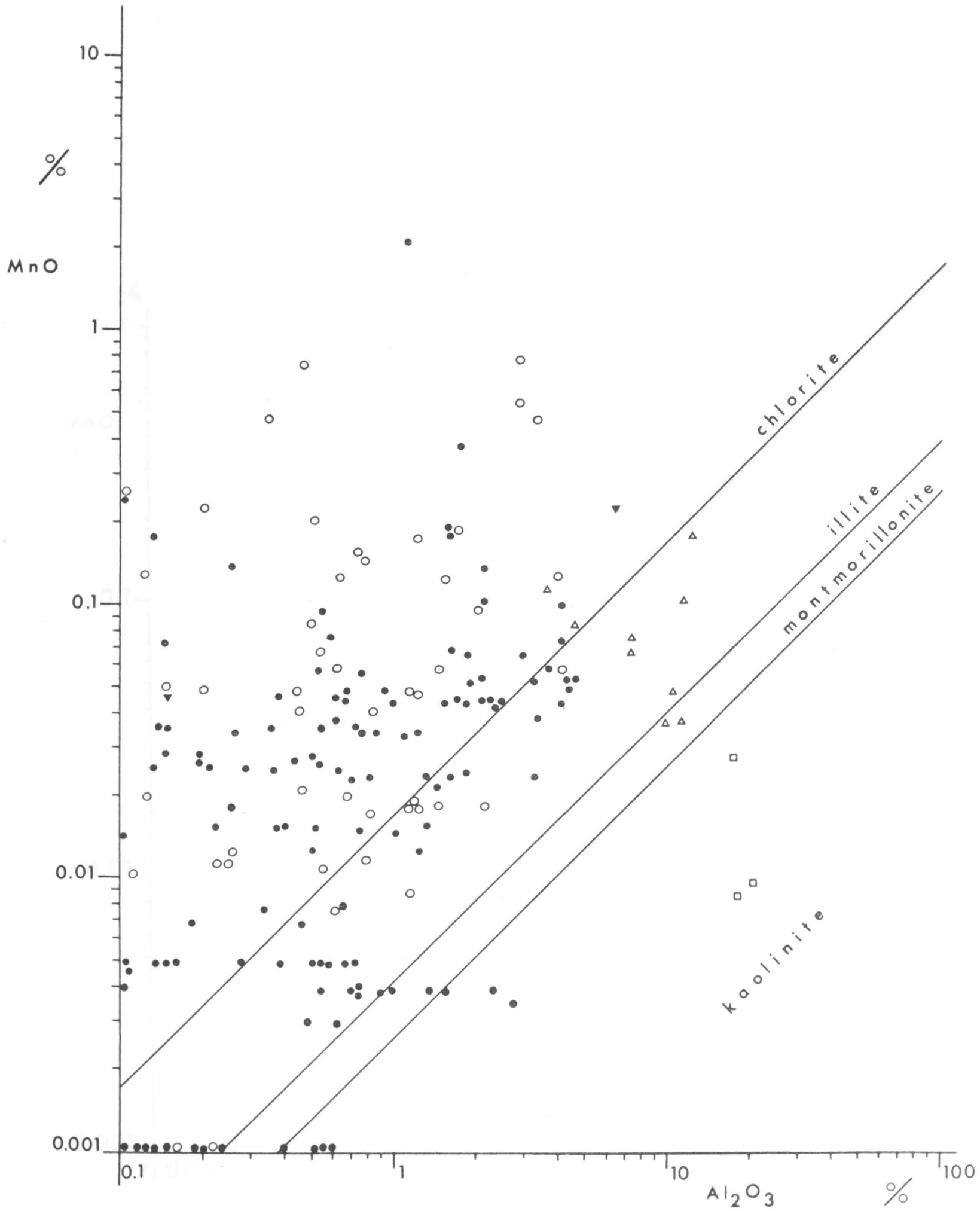
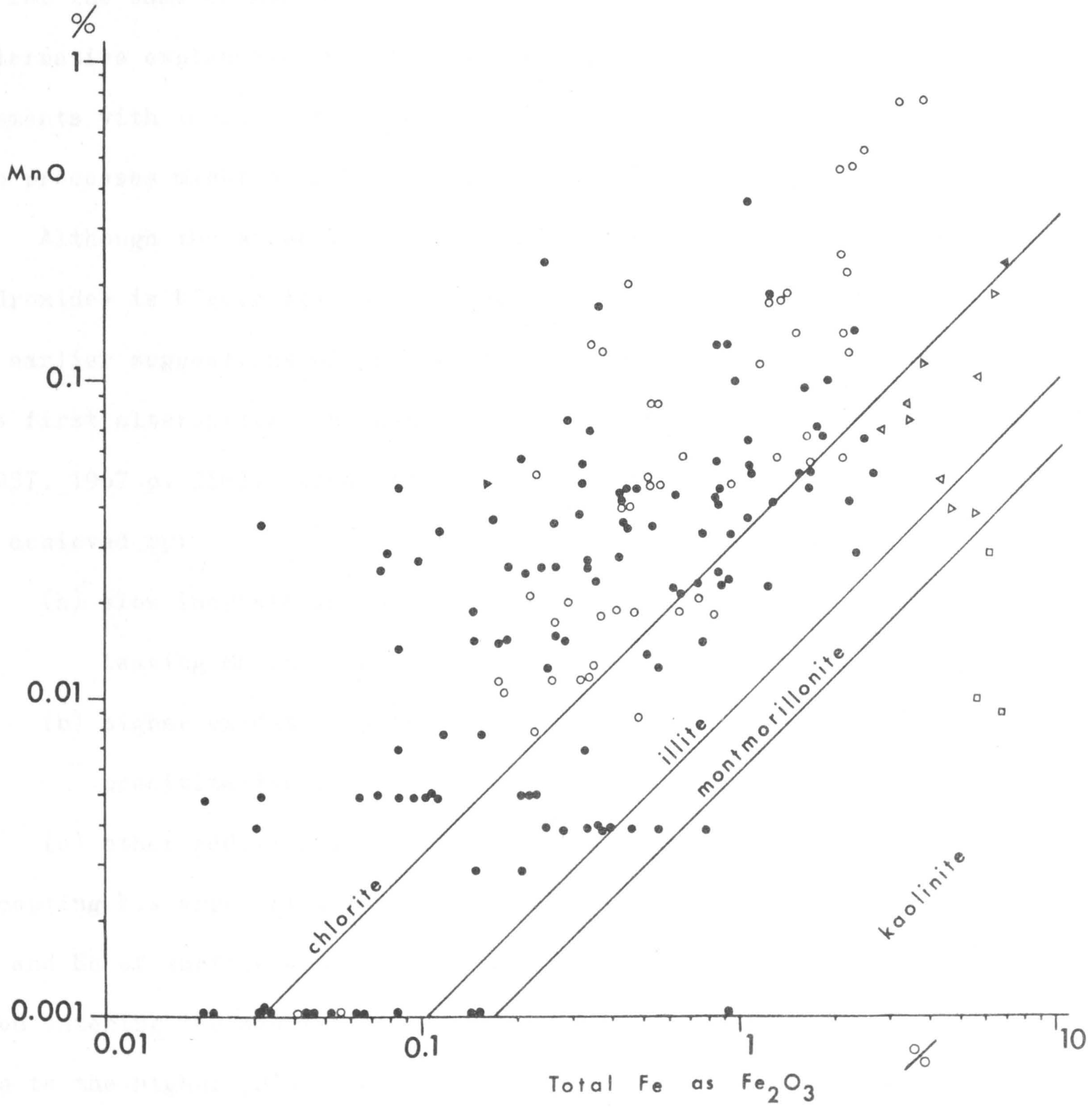


Figure 15. Scatter diagram of MnO vs. Total Fe.
Explanations as in figure 5.



their linear correlation coefficient (+0.437) is still high. This would point to some degree of their geochemical fractionation.

There is a comparatively higher fractionation of Mn than Fe into early diagenetic dolomites as well as a stronger Mn response to the changes in climatic conditions in post-Cambrian rocks (fig. 13).

Assuming that the factors affecting solubility of Fe are applicable to Mn as well, this would mean more rapid increase in solubility of Mn than Fe for the same change of conditions (incongruent dissolution). An alternative explanation might be a decrease in the separation of these two elements with their increasing solubility and total transport load. These two processes might have been complementary.

Although the solubility of Mn carbonates, sulphides, silicates and hydroxides is higher than of the corresponding Fe compounds, and in spite of earlier suggestions of preferential leaching of Mn by various authors, the first alternative (incongruent dissolution) is questioned by Krauskopf (1957, 1967 p. 266). According to Krauskopf the separation of Fe and Mn is achieved by:

(a) slow increase in pH causing earlier precipitation of Fe and leaving Mn in solution,

(b) higher oxidation potential of Fe causing its earlier precipitation due to the formation of Fe oxides,

(c) other additional factors, such as bacteria, etc.

Accepting his arguments, it would mean that during humid periods the lower pH and Eh of surface waters would increase solubility of both elements. Upon entering the sea the separation of Mn from Fe might be less complete due to the higher pH gradient. An alternative, or additional, explanation might be the lower Eh (P_{O_2}) of such marginal basins during humid periods. This would enable even Fe to be held in solution for longer periods and

its transport into deeper parts of the sea. Both processes might lead to higher Mn/Fe ratios in near-shore sediments.

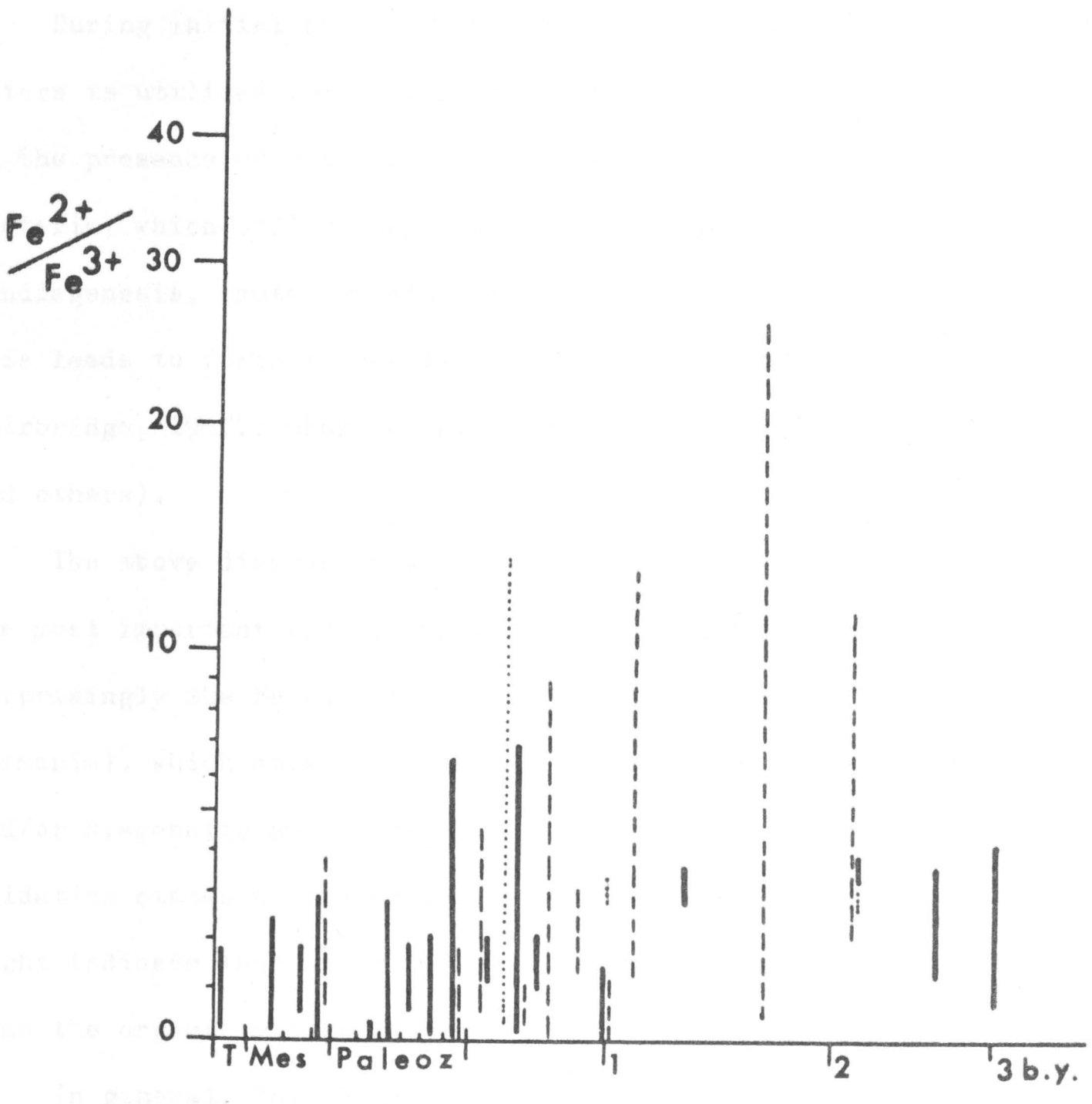
It is however quite possible, that due to the higher solubility of Mn compounds a decrease in Eh and pH of surface waters would lead not only to the increase of the total load of both elements, but also to a proportionally higher solubility of Mn. The increased Mn/Fe ratios during humid periods might then be explained simply as a feature of continental waters. This might be supported by the observation that Fe^{2+} is a reducing agent with respect to higher valent Mn oxides (Stumm and Morgan, 1970 p. 546) and so with decreasing Eh the soluble Mn^{2+} will be present before Fe^{2+} in the waters of an aquifer.

7.12 Fe^{2+}/Fe^{3+}

The reduction (or oxidation) state of the rocks as expressed by the Fe^{2+}/Fe^{3+} ratios shows a positive correlation with the Mg or $(Mg/Ca) \times 10^2$ (fig. 4 and Table 3). This would indicate a lower oxidation state of dolomites. The difference in the oxidation state is predominantly the result of diagenetic and age factors, since the dolomites form major part of Precambrian and limestones of Phanerozoic sequences. The problem will be discussed later (Chapter 8).

Comparing different types of rocks in contemporaneous sequences (fig. 16), the lower oxidation state of dolomites is not so evident. The Triassic limestones of the Western Carpathians have average Fe^{2+}/Fe^{3+} ratio 0.930 (range 0.045-2.923), whereas the average value for dolomites is 2.215 (range 0.859-3.817). The values for dolomites in the Cambrian sequence are completely within the range of limestones. The above discussion indicates either slightly lower (by a factor of 2) or equivalent oxidation state of dolomites in contemporaneous rocks. Siltstones and mudstones of the

Figure 16. Ranges of Fe^{++}/Fe^{+++} ratios of contemporaneous rocks.
Explanations:
(1) limestones, (2) dolomites, (3) siltstones, mudstones and silicites.



Adelaidean geosyncline show slightly lower oxidation state than carbonates (average Fe^{2+}/Fe^{3+} 4.401 vs. 2.458), but the overlap of data is considerable. The range is 0.644-13.598 in siltstones and mudstones and 0.070-9.000 in carbonates. The above description would indicate a decrease of oxidation state in the order limestones $\geq$ (early diagenetic) dolomites $\geq$ siltstones and mudstones. This may be a reflection of the availability of oxygen in a given sedimentary environment, or more likely of its abundance during diagenetic processes.

During initial stage of syndiagenesis the dissolved oxygen in pore waters is utilised for decomposition of organic matter by aerobic bacteria. In the presence of chemically bound oxygen (SO_4 etc.) the anaerobic bacteria, which utilise organic matter during early burial stage of syndiagenesis, cause reduction of oxygen bearing anions and also of Fe. This leads to further decrease in the oxidation state of iron (cf. Fairbridge, 1967b; Ghose et al., 1970; Kaplan et al., 1963; Berner, 1964 and others).

The above discussion would point to the presence of organic matter as the most important factor influencing the oxidation state of iron. Surprisingly the Fe oxidation states of Gordon Limestones (Ordovician, Tasmania), which show the strongest features of an "euxinic" sedimentary and/or diagenetic environment, are equal or only slightly lower than the oxidation states of the well aerated sequences of the Cambrian age. This might indicate that other factors are in some instances more effective than the organic matter content.

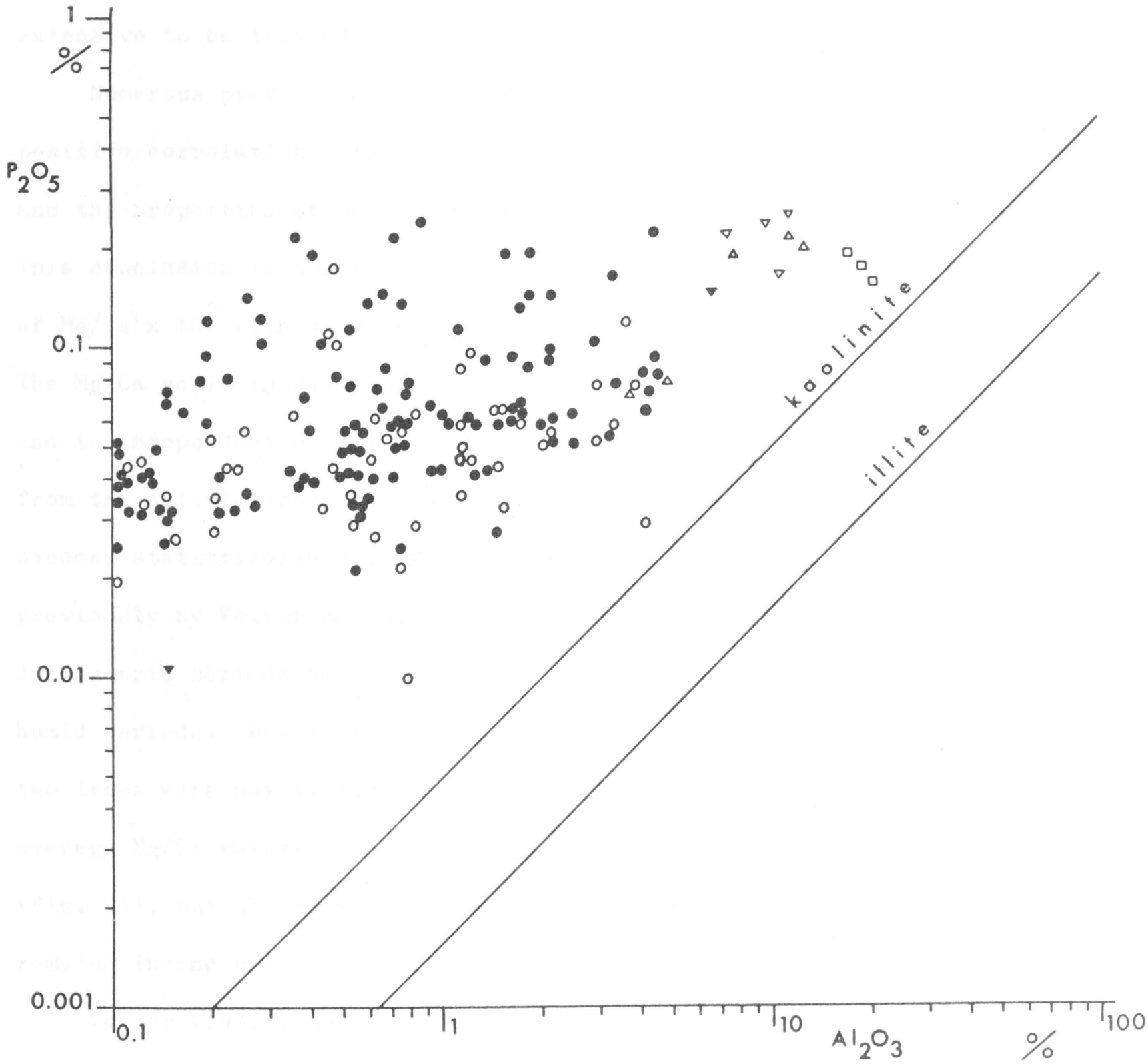
In general, for Phanerozoic rocks, the reef-like and organodetrital limestones and often also late diagenetic dolomites contain Fe^{2+}/Fe^{3+} ratios <1. Limestones with features of a partly "euxinic" environment and/or higher content of insoluble residue are averaging between 1-2.

Devonian stromatolitic limestones (Cavan Bluff Limestones), limestones from Cambrian and Triassic intertidal and lagoonal environments and early diagenetic dolomites are averaging about 2 or higher. This observation suggests that insoluble residue content and thus porosity and permeability of the rocks is the main factor controlling the oxidation state of iron. This explanation would also be consistent with the high correlation coefficient of Fe^{2+}/Fe^{3+} with SiO_2 and Al_2O_3.

7.13 PHOSPHORUS

The correlation coefficient of P_2O_5 and Al_2O_3, although statistically significant, is very likely due only to the simultaneous presence of aluminosilicates and phosphates. The highest correlation coefficient of P_2O_5 with TiO_2 (Table 3) as well as the higher concentrations of P in siltstones than mudstones would indicate association of P with a coarser aluminosilicate fraction, very likely in a form of apatite. The association of Ca-phosphates and carbonates on outer shelf areas is well known (Müller, in Füchtbauer and Müller, 1970; Krauskopf, 1967). A somewhat higher P_2O_5 content of limestones, compared to dolomites, is indicated by the scatter diagram (fig. 17) as well as by the high positive skewness of the limestone histogram (fig. 3). This may be explained either by greater substitution of Ca-phosphate and $CaCO_3$ (carbonate-apatite), or more likely by simultaneous precipitation of those two phases on the open shelf of the sea. The majority of the Ca-phosphates are precipitated from solution before high pH values typical for dolomite sedimentary environments are reached (Krauskopf, 1967 p. 92). High pH environments are also notably deficient in organic production and so are not very favourable for organic phosphorus concentration.

Figure 17. Scatter diagram of P_2O_5 vs. Al_2O_3. Explanations as in figure 5.



7.14 CALCIUM AND MAGNESIUM

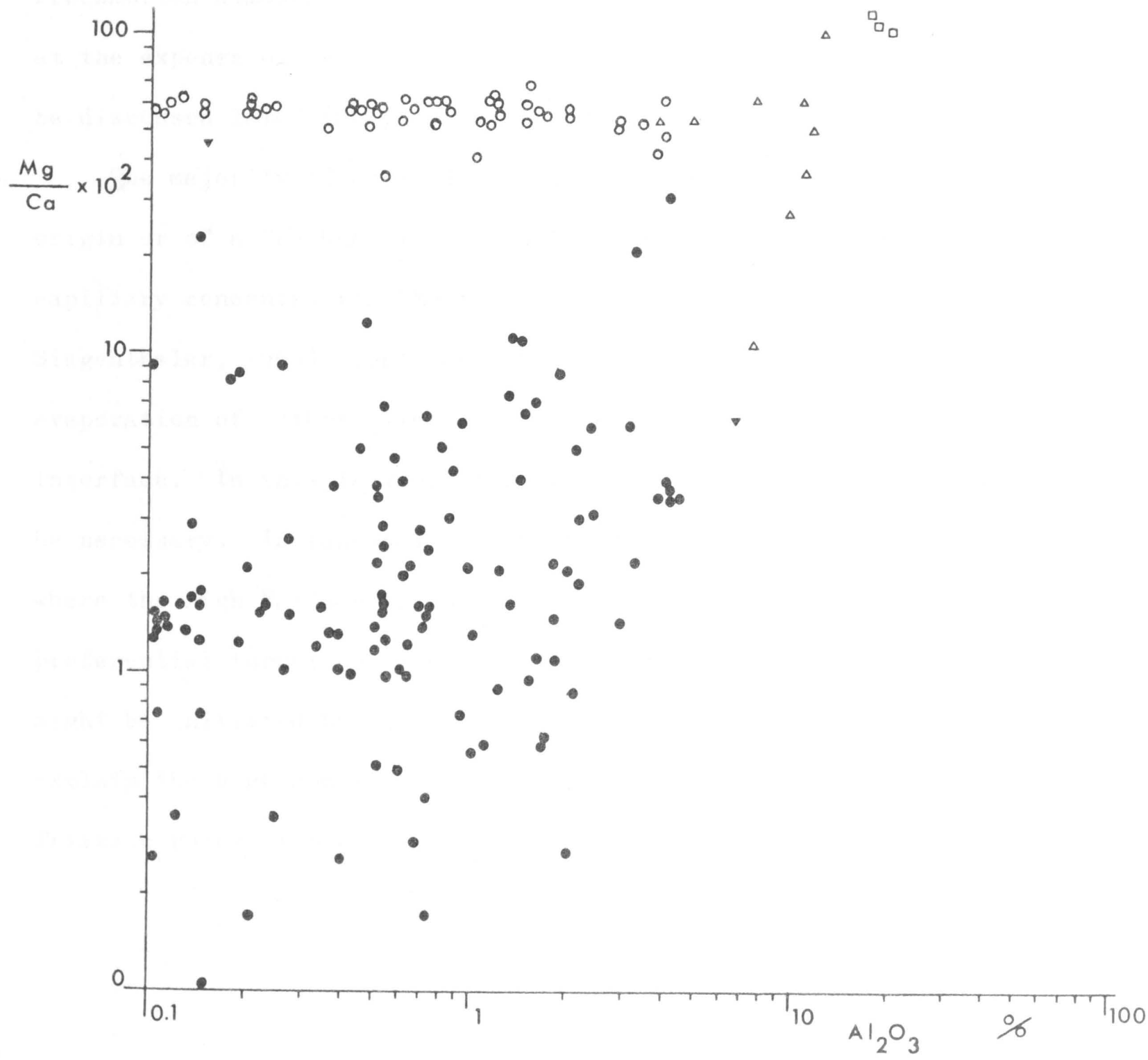
The distribution of these two major cations of carbonate rocks has already been discussed (p. 41).

There are many publications dealing with the petrology of carbonate rocks (cf. Chilingar et al., 1967) and discussion of them is outside the scope of this thesis. Similarly the problems of dolomitization are too extensive to be treated in this discussion.

Numerous previous authors (cf. Fairbridge et al., 1967) have observed positive correlation between insoluble residue content of carbonate rocks and the proportion of dolomites in the carbonate sequences (cf. p. 43). This conclusion is not supported by the insignificant correlation coefficient of $(Mg/Ca) \times 10^2$ with Al_2O_3 for the whole group of carbonate rocks (Table 3). The Mg/Ca ratio in dolomites is in fact close to the stochiometric values and is independent of clay content (fig. 18). However, excluding dolomites from the calculations, the correlation coefficient of Mg/Ca with Al_2O_3 becomes statistically significant (+0.315). This relation was observed previously by Veizer and Demovič (in press). In their data, rocks deposited during arid periods had higher Mg/Ca ratios than rocks deposited during humid periods. Due to the small number of rock types, the slopes of these two lines were not statistically significant. In the present data, the average Mg/Ca values for arid periods are higher than for humid ones (fig. 31), but the scatter is considerable and so the argument still remains inconclusive.

Veizer (1970a) postulated, that the average clay content of early diagenetic dolomites is higher than of any other carbonate rock type. He argued that the clay particles might serve as a charged net membrane or seeds for interstitial solutions with high Mg/Ca ratios, thus causing dolomite formation around clay centres. Similar arguments were advanced

Figure 18. Scatter diagram of (Mg/Ca) x 10^2 vs. Al_2O_3. Explanations as in figure 5.



earlier by Schmidt (1965), Kahle (1965) and possibly by other authors, but with no clear specification of the kind of dolomites involved.

Although the majority of samples studied here are early diagenetic dolomites, the correlation of Mg or Mg/Ca with Al_2O_3 is not statistically significant. This would mean that the correlation is valid for some kinds of early diagenetic dolomites only. Whether the different P_{CO_2} of Precambrian atmosphere was sufficient for preferential formation of dolomite at the expense of calcite (aragonite) is not yet clear. The problem will be discussed later (Chapters 8 and 12).

The majority of early diagenetic dolomites are of intertidal algal origin or of a "sabkha" type (Chapters 2 and 3). In such environments the capillary concentration (Mueller, 1960) or evaporative pumping (Hsü and Siegenthaler, 1969) might cause dolomitization of the surface layer by evaporation of interstitial water with high Mg/Ca ratio at the sediment-air interface. In this instance the role of catalysing clay minerals would not be necessary. In lagoonal sequences with thick sediments of aragonite, where the high Mg/Ca solutions are squeezed out by load pressure, the preferential formation of early diagenetic dolomites in clay rich layers might be initiated by the smaller permeability of such layers. This might explain the high content of clays in such rocks, as observed for the Triassic rocks of the Western Carpathians (Veizer, 1970a).

Chapter 8

VARIATIONS OF ELEMENT ABUNDANCES WITH TIME

8.1 INTRODUCTION

Several trends are immediately apparent when element abundances are plotted against geological age. In particular CaO, Sr and Na_2O decrease and MgO, total Fe and MnO increase with the age of the rocks. There are no obvious trends for K_2O and SiO_2 and the fluctuations in Al_2O_3, Rb and TiO_2 are quite random (figs. 19-22), related inversely to the total carbonate content (CO_2).

These trends are more obvious after normalization to Al_2O_3, since the clays are the carrier phases for all elements, except Ca and Sr, and Al_2O_3 is also the least soluble species.

I am aware that the calculated averages may not be representative because of insufficient data, but the agreement with previously published data for the Russian Platform and North America strongly supports the validity of those trends. Thus, although the slope of a particular curve may be questioned, its general sign is very likely correct.

Possible factors causing this chemical evolution might be summarised into five categories:

(a) diagenetic effects,

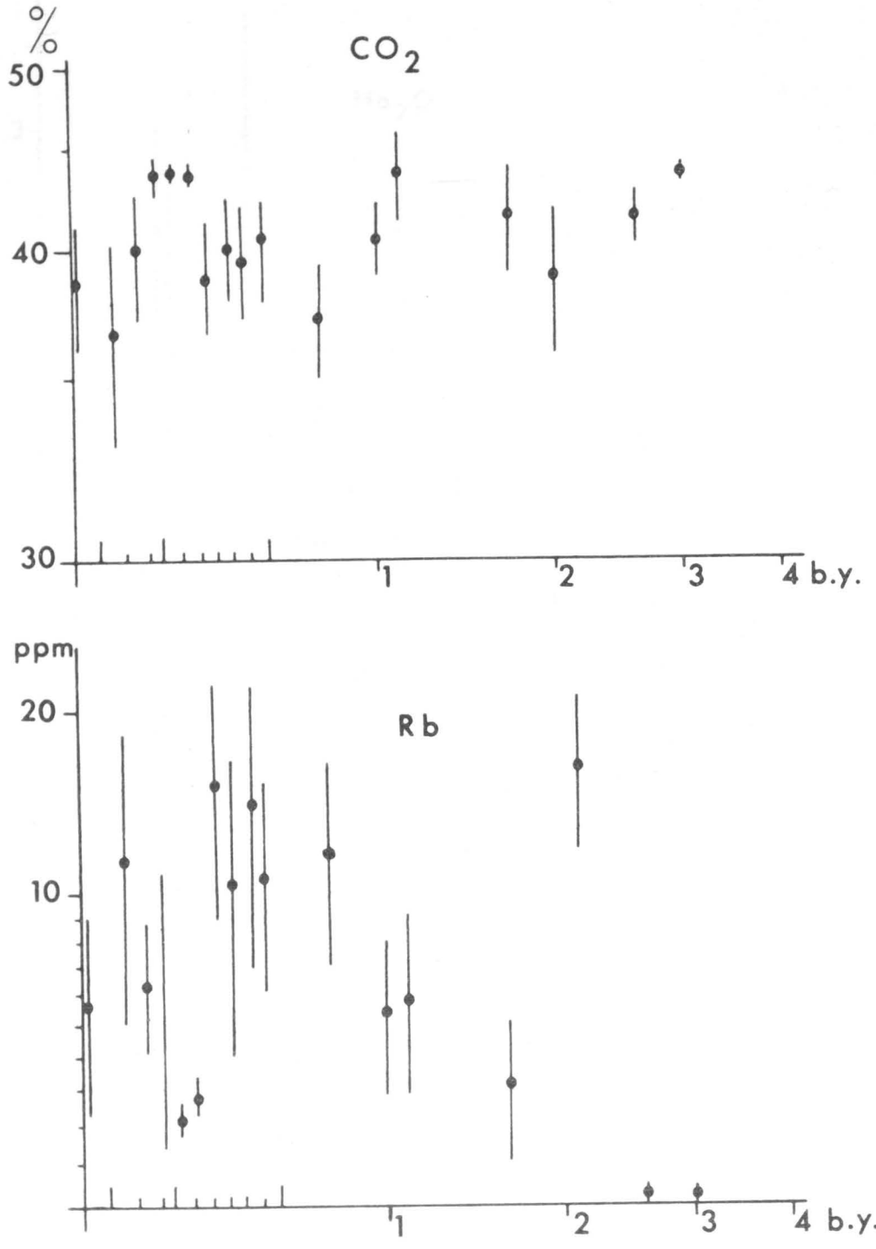
(b) progressive evolution of sedimentary environments and their associated sedimentary rocks,

(c) changes in chemical composition of the atmosphere and the hydrosphere,

(d) changes in chemical composition of the upper continental crust which serves as a source region for sedimentary rocks,

(e) other factors.

Figure 19. Variations of CO_2, Rb and SiO_2 with geological age.
Explanations: Vertical bars represent 1σ limits of the mean.



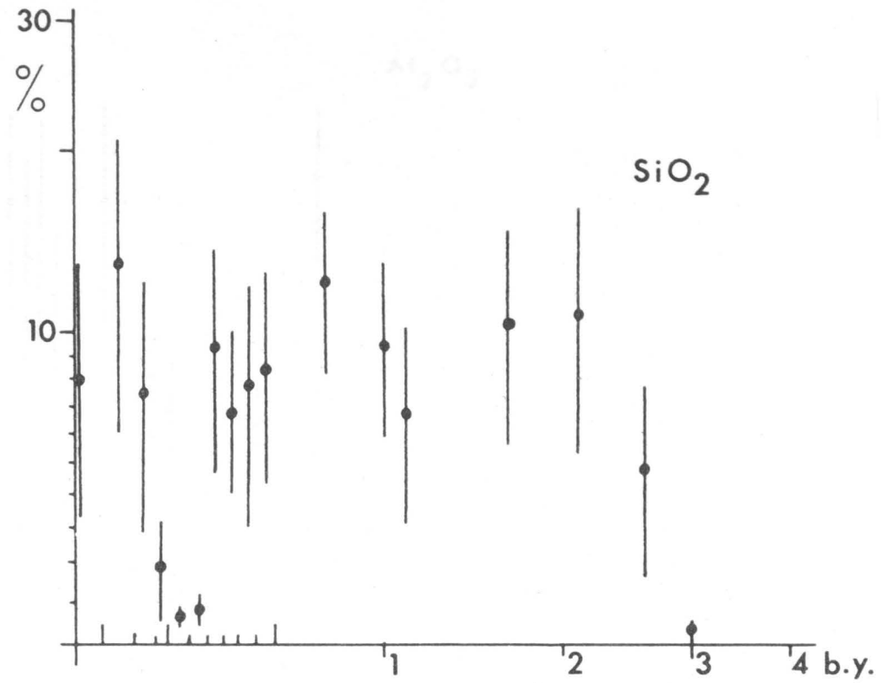
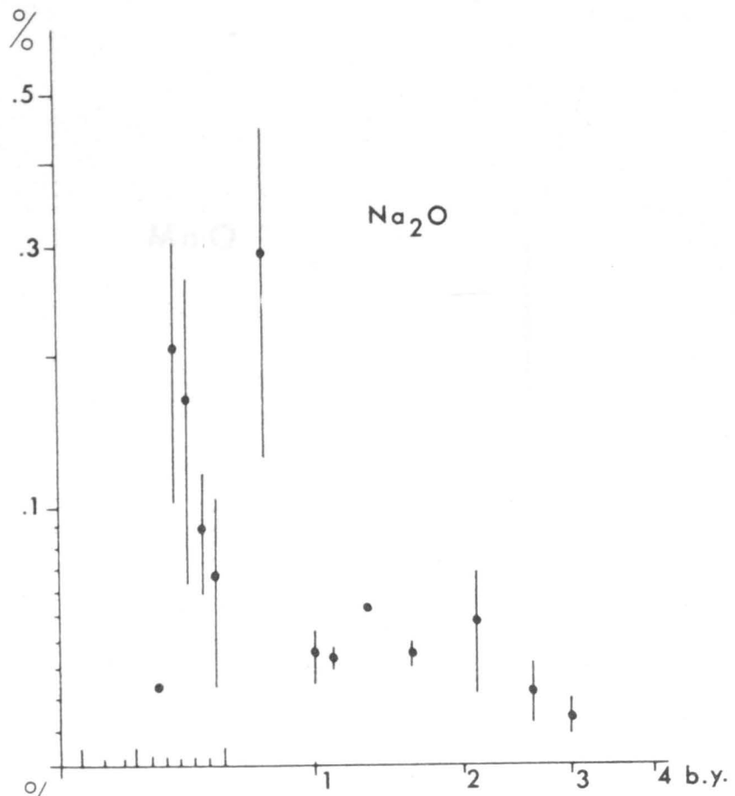
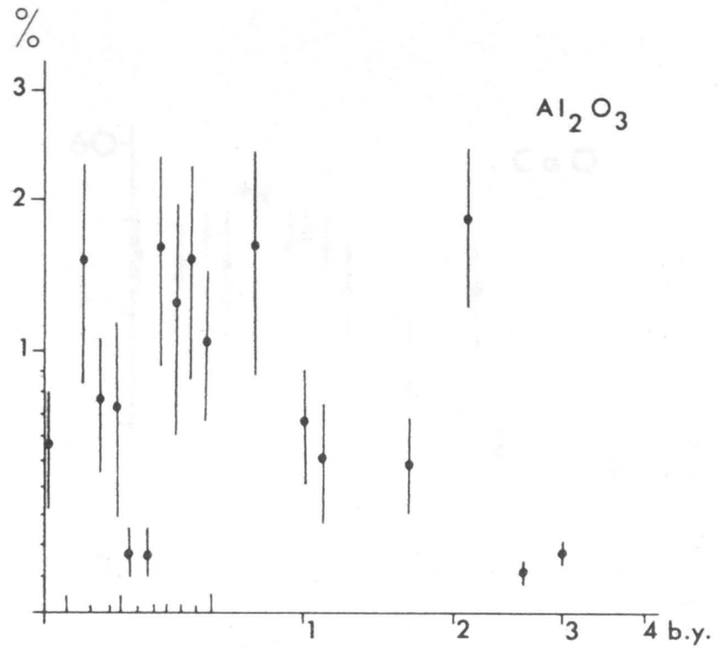
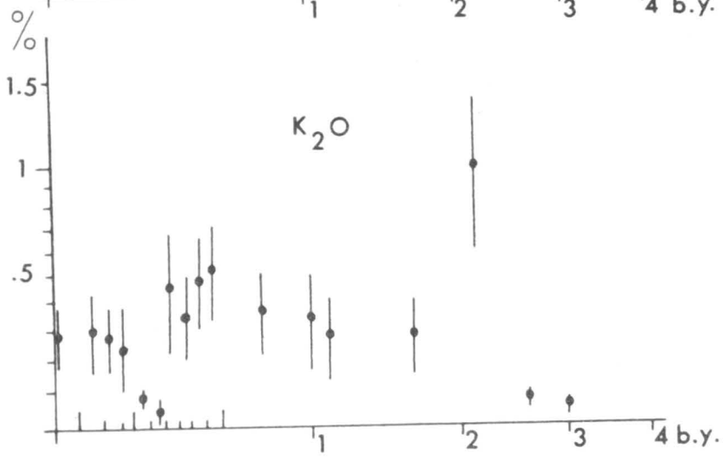


Figure 20. Variations of Na_2O, K_2O, Al_2O_3 and TiO_2 with geological age.
Explanations as in figure 19.







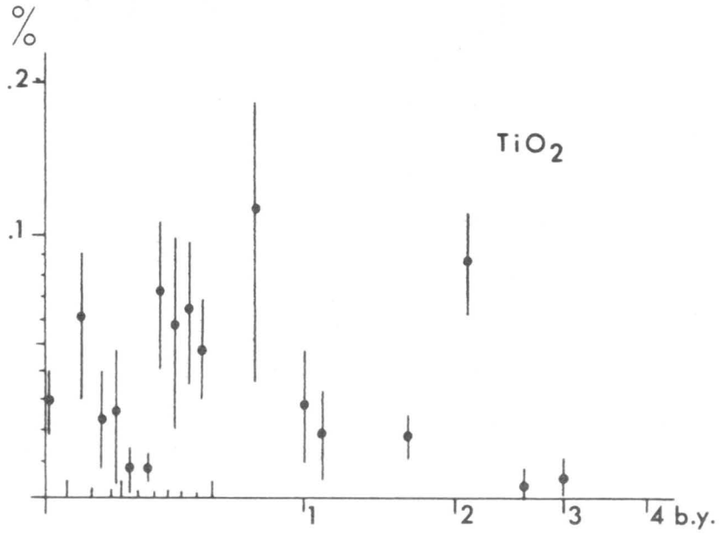


Figure 21. Variations of MnO, CaO and MgO with geological age.
Explanations as in figure 19.

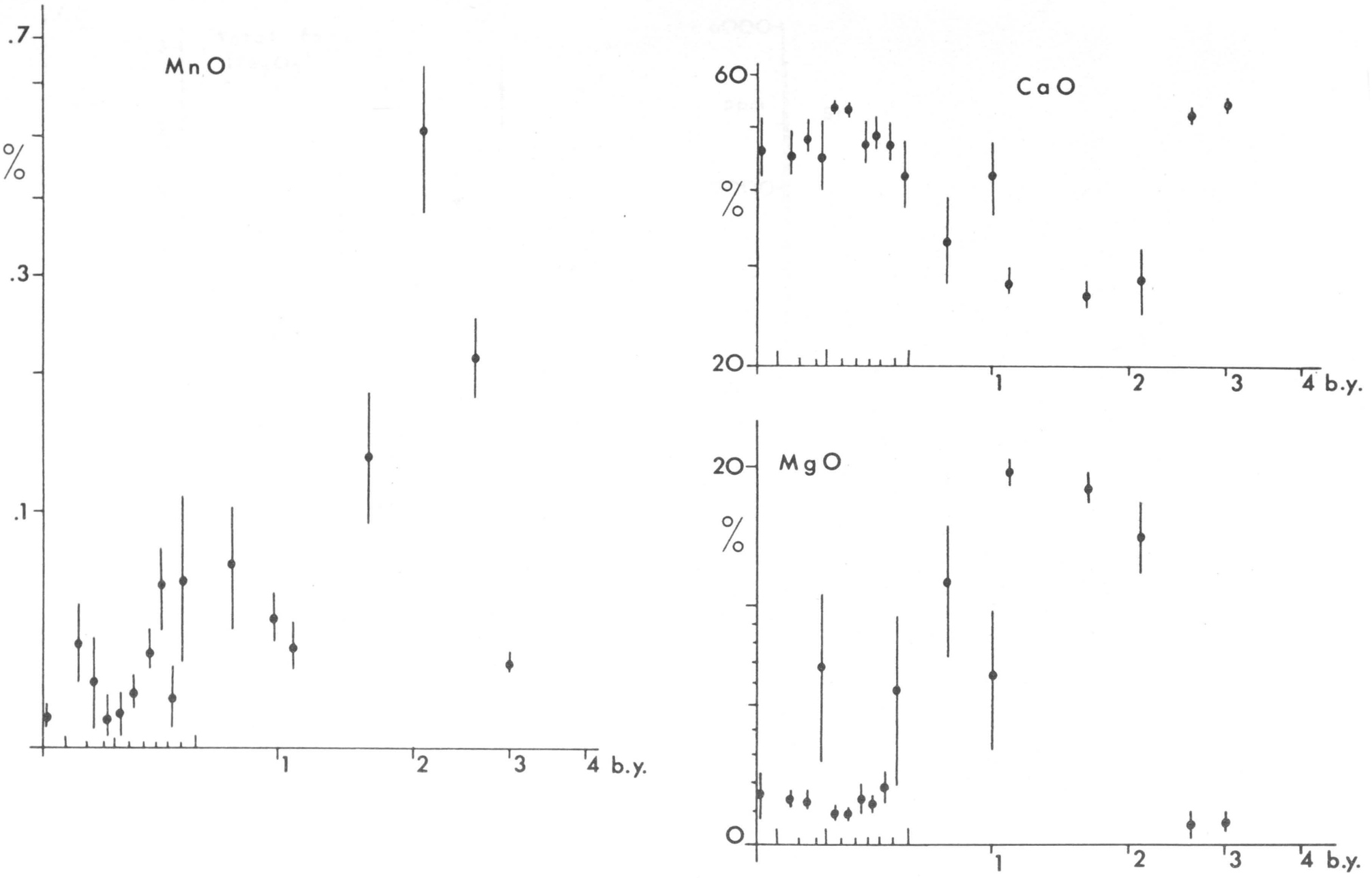
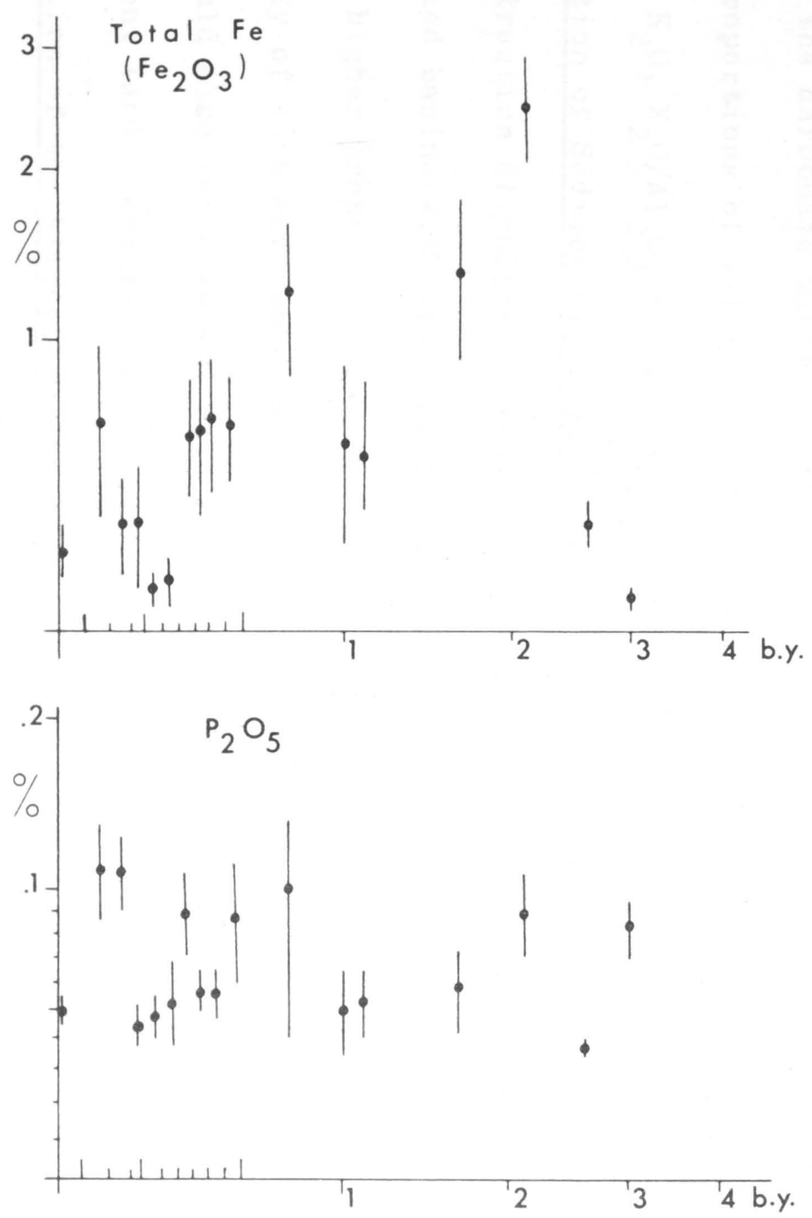
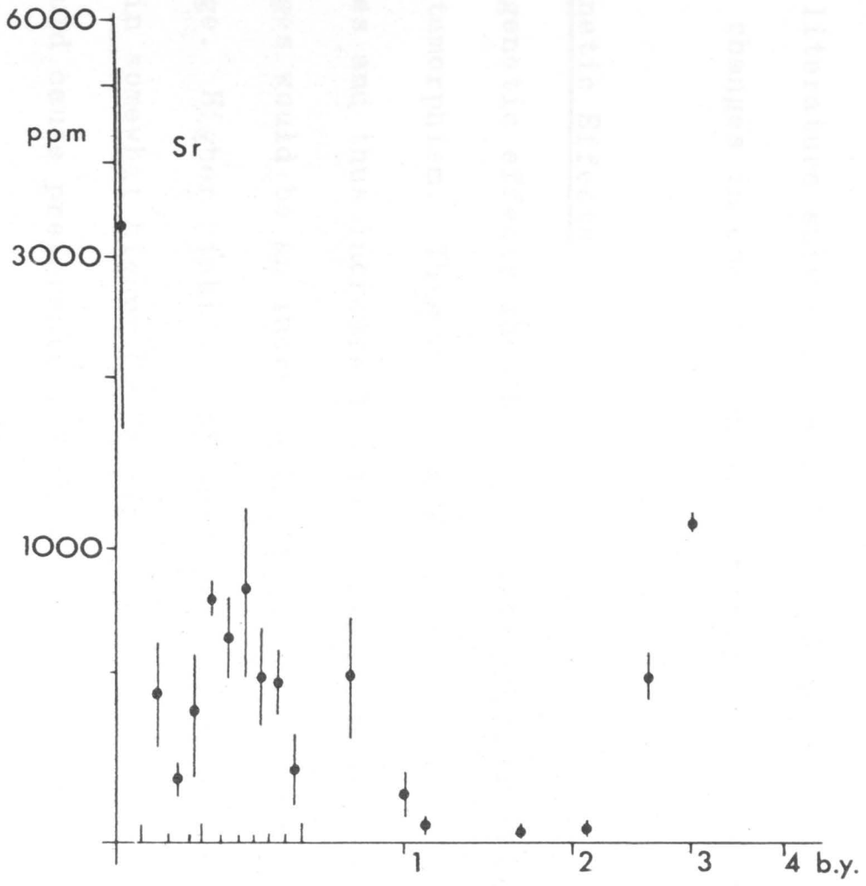


Figure 22. Variations of Total Fe, P_2O_5 and Sr with geological age. Explanations as in figure 19.





In the majority of cases all the above listed factors were partially responsible for development of those trends. The following discussion will be thus devoted mainly to the determination of priority for each particular element.

From a literature survey it is possible to predict, to a certain degree, the chemical changes in composition of carbonate rocks due to the above listed factors.

8.1.1 Diagenetic Effects

The diagenetic effects should, to a first approximation, act as a low degree of metamorphism. This would cause preferential solution of the more soluble phases and thus increase the insoluble residue content. A consequence of such changes would be an increase in Al_2O_3 content of the rocks with increasing age. Higher stability of dolomite, compared to calcite, might also result in somewhat higher Mg/Ca ratio of older rocks. Increasing burial pressure should cause preferential "expulsion" of impurities from lattice positions of the carbonate minerals (Sr) and reduction of Fe^{3+} to Fe^{2+}. Increasing proportions of illites in older rocks (cf. p. 71) should lead to increases in K_2O, K_2O/Al_2O_3 and K_2O/Na_2O and decreases in Na_2O and Na_2O/Al_2O_3.

8.1.2 Evolution of Sedimentary Environments

The contraction of carbonate sedimentary environments to progressively more restricted basins with increasing age (see Chapter 3) should lead to the increasingly higher proportion of dolomites in older sequences. The susceptibility of such environments to the influx of continentally derived elements should also increase and this might result in higher insoluble residue content (and elements associated with it) in older rocks.

8.1.3 Evolution of the Atmosphere and Hydrosphere

There is a good deal of controversy concerning the evolution of the atmosphere and hydrosphere. The fractionation of the crust, hydrosphere and

atmosphere is very likely related to the general evolution of the earth's mantle (Ringwood, 1969; Vinogradov, 1967, 1968; Rubey, 1951, 1955; Urey, 1959 and others). The majority of authors consider that the gravitational fields during the agglomeration of the Earth from planetesimals was too small to retain the primordial atmosphere and hydrosphere. Thus the present atmosphere and hydrosphere would be a secondary product of the degassing of the earth's mantle, possibly through volcanic activity.

The history of the atmosphere and hydrosphere during the interval from 4.6-3.5 b.y. ago is known only from various theoretical considerations, but no direct evidence is available.

Whether the early atmosphere was strongly reducing and composed of substantial amounts of CH_4, NH_3, H and other species, or was formed by CO_2, N_2, H_2S and possibly CO is a matter of speculation (Rubey, 1951, 1955; Holland, 1962, 1964; Miller and Urey, 1959; Oparin, 1961; Vinogradov, 1967; Rasool and McGovern, 1966 and others). From our point of view it is possible, to a certain degree, to neglect this controversy, since the time scale considered is only from about 3.2 b.y. until present. In this case the composition of volcanic gases and contemporaneous atmosphere would be very likely similar to the latter alternative, regardless of its original state. Its probable composition might be similar to the second stage model of Holland (1962). The role of CO_2 instead of CH_4 for the atmosphere-hydrosphere system in periods older than 3 b.y. was advocated also on the basis of C isotopic data in carbonate rocks (Galimov et al., 1968).

The table (No. 4) of atmospheric composition as formulated by Holland (1962) is presented below.

Table 4. Composition of the earth's atmosphere (Holland, 1962)

	Stage 1	Stage 2	Stage 3	Partial pressures in Stage 2 (atm.)	
Major components	CH_4	N_2	N_2	N_2	$0.01 < P < 0.08$
$P > 10^{-2}$ atm	$H_2(?)$		O_2	H_2O	$3x10^{-4}$ to $3x10^{-3}$
Minor components	$H_2(?)$			CO_2	approx. $3x10^{-4}$
$10^{-2} > P > 10^{-4}$	H_2O	H_2O	Ar	Ar	$10^{-4} < P < 10^{-2}$
	N_2	CO_2	H_2O	Ne	$10^{-6} < P < 10^{-4}$
	H_2S	Ar	CO_2	He	$10^{-6} < P < 10^{-4}$
	NH_3			CH_4	$10^{-6} < P < 10^{-4}$
	Ar			NH_3	tr
Trace components	He	Ne	Ne	SO_2	tr
$10^{-4} > P > 10^{-6}$		He	He	H_2S	tr
		CH_4	CH_4	O_2	non-equilibrium state
		$NH_3(?)$	Kr		
		$SO_2(?)$			
		$H_2S(?)$			

From this table it is obvious that for the second and third stages oxygen and CO_2 were the two most important gases in so far as chemical weathering, transport and sedimentation were concerned. So it would be of interest to set possible limits for their partial pressures in geologic history (Archean to present).

CO_2 is the stable species in volcanic gases in equilibrium with a Fe^{2+}/Fe^{3+} buffer system. Holland (1962) calculated that P_{CO_2}/P_{CO} of such

gases would be about 37. There is a kind of exogenic buffer system which at least partially limits P_{CO_2} in the atmosphere. This system involves the rate of weathering, organic production and sedimentation and is to some extent self-regulating. The prime role in this buffering system is played by Mg-carbonates and Mg-silicates (Holland, 1968). According to Holland (1965) Mg-carbonates are unstable with respect to Mg-silicates at $P_{CO_2} < 10^{-4}$. At $P_{CO_2} < 10^{-3.7}$ gypsum would be stabilized against $CaCO_3$ in the open ocean (Holland, 1965; Stumm and Morgan, 1970, p. 417). Since gypsum is not known from the open sea facies and dolomite is present in sedimentological record since at least 3 b.y. ago, the P_{CO_2} was probably not below its present value ($10^{-3.5}$). The above discussion is valid for a silicate + carbonate buffered ocean (see p. 68). Rubey advocated a similar lower limit for a carbonate-buffered ocean on the basis of the stability fields of brucite and dolomite.

It is more difficult to estimate the upper limit. Rubey (1951) showed that P_{CO_2} would be very unlikely above 1 atm., and possibly not more than 20-30 times higher than the present value. Holland (1968) maintains that since the Silurian, P_{CO_2} has not been higher than about 4 times of its present value, because the increased assimilation of land plants would increase weathering efficiency and the system would be equilibrated. Before the Silurian, due to the lower weathering efficiency, P_{CO_2} might have been higher, but not more than 10-100 times of its present value. According to Garrels and MacKenzie (1971a, p. 294) the internal P_{CO_2} of the aqeous system in equilibrium with siderite and greenalite (banded iron ore formations) is about $10^{-2.5}$.

Judging from the above discussion, the probable variations in atmospheric P_{CO_2} for the last 3 b.y. were within the $10^{-3.5}$ and $10^{-2.5}$ (10^{-2}) limits, with P_{CO_2} increasing towards older periods.

There is also quite extensive literature about the evolution of oxygen in the earth's atmosphere. There is general agreement that oxygen in its present quantities could not have come in a free state from the earth's interior. P_{O_2} in equilibrium with a Fe^{2+}/Fe^{3+} buffer system in basaltic melts would be of the order 10^{-7} (Holland, 1964). Two processes have been postulated to explain the quantities of oxygen present in the modern atmosphere (P_{O_2} = 0.21 atm.). These are the photodissociation of H_2O by UV radiation, or the photosynthetic activity of organisms. According to calculations of Berkner and Marshall (1964) photodissociation in the absence of substantial organic activity would establish P_{O_2} equilibrium slightly below 0.001 of PAL (present atmospheric level) and so the P_{O_2} of the Archean should be around 10^{-4} atm. Their calculations were questioned by Brinkman (1969). He concluded that this process might lead to P_{O_2} values as high as 0.25 of PAL. There are, however, strong indications, although not conclusive, of a principally non-oxygenic atmosphere in the early stages of the earth's history. The geological arguments were summarised by Rutten (1962, 1966). Holland (1962) argued that oxygen during his second stage of atmospheric evolution was present only in non-equilibrium quantities. On the basis of stability fields of U_3O_8-UO_3 it might have been below 10^{-21} atm., but the argument is not conclusive because the rate of oxidation might have been slow compared to the rate of formation of the pitchblende detrital grains. So it is difficult to set a lower limit to the P_{O_2} during Archean period, but possibly Holland's suggestion of non-equilibrium quantities might be accepted. The upper limit is not very likely to be much above the present atmospheric level, since the high production of O_3 would prevent UV radiation from forming anti-rachitic vitamin essential for organisms (Stetson, 1942, in Rubey, 1951). It is not likely that the P_{O_2} during Phanerozoic ever exceeded the total atmospheric pressure and thus P_{O_2} was probably always below 1 atm. Since the P_{O_2} was

very likely decreasing towards older periods, the partial pressure of 1 atm. may be regarded as a probable upper limit. The possible rate of the increase in P_{O_2} from Archean to present will be discussed later in the text.

The composition of the atmosphere is only one variable in the geological record. Another important system is the hydrosphere. The volume of the ocean is a factor which would influence most of the other considerations. Possible hypotheses were summarised by Mason (1966, p. 204). If the rate of outgassing of excess volatiles is proportional to the rate of sialic crustal fractionation (Rubey, 1951; Vinogradov, 1968; Kushiro, 1970), then the alternative of Kuenen (1950) seems to be the most likely one. As will be discussed later (p.129), there is evidence that a high proportion of sialic crust was fractionated earlier than about 2.5 b.y. ago. This would indicate that approximately half of the present oceanic volume was already in existence at this time. The growth of the total volume might have been gradual and much slower in younger periods.

If we assume that for all practical purposes the volume of the ocean has grown only slowly since say the end of Archean, another problem which arises is the composition of this hydrosphere. The essential argument of Rubey's (1951) hypothesis is that the composition of ocean was more or less similar to what it is at present. If on the other hand the ocean originated by condensation of a primordial atmosphere, salinity would increase with time. The problem depends on the nature and composition of the early atmosphere as mentioned at the beginning of this chapter.

According to Sillén (1961) "the ocean is the result of a gigantic acid-base titration. Acids that have leaked out from the earth are titrated with bases that have been set free by the weathering of primary rocks". In other words the ocean is some kind of equilibrium product of excess volatiles (Rubey, 1951) with silicates. The ocean seems to be approximately saturated and

its composition, at least at present, is probably dominated by a steady state system (Sillén, 1961; Krauskopf, 1967 p. 623; Holland, 1965; Siever, 1968; Stumm and Morgan, 1970 p. 413; Garrels and MacKenzie, 1971a, p. 279). The composition of the ocean is thus "buffered" by silicates, carbonates, salts and silicites (Siever, 1968). Once a composition similar to present sea water is achieved, it is very difficult to alter it (Kramer, 1965; Holland, 1965; Garrels and MacKenzie, 1971a). If this "equilibrium" state is maintained today, it is plausible to assume that it was operating also in the geological past, although one has to admit that this assumption may be questioned. The geological, sedimentological and organic record (cf. Ronov, 1964) seems to be consistent with such an assumption at least since the end of the Archean.

So if the composition of the degassed substances and composition of the weathered crust have remained at least approximately constant, the composition of the atmosphere-hydrosphere in a steady state system should also be stable.

With exception of some secular variations and small degree of evolutionary changes, the preceding and following discussion suggests that the above statement might be permissible on a large scale. The probable exceptions from this pattern were P_{O_2} and P_{CO_2} and possibly Cl^-. So the "equilibrium" state of the ocean composition was probably evolving in response to the changing CO_2 and O_2 content of the atmosphere and Cl^- content (?) of the hydrosphere. This might in turn influence the oxidation state of some cations and anions and so their solubilities. It might also influence the solubilities of carbonates (and chlorides?).

It is beyond my abilities to predict possible changes due to the above factors. The possible consequences can only be calculated by a physical chemist (cf. Holland, 1965). The changes will also depend to a certain degree on the availability of particular elements supplied by weathering.

There are two additional variables which might have strong influence on the chemistry of the ocean. These are pH and temperature.

The controversy about major buffering system with respect to pH in recent oceans is well known (see Pytkowicz, 1967; Sillén, 1961; Garrels, 1965; Holland, 1965; Siever, 1968; Krauskopf, 1967 p. 621 and others). In this thesis it is assumed that silicates are the major long term determining factor, whereas carbonates due to their faster response take care of short term fluctuations and so both systems are complementary (Stumm and Morgan, 1970 p. 418). This situation might have been active at least since the end of the Archean when carbonates began to occur frequently in the sedimentary column. If true, this would severely limit possible pH fluctuations of the oceans. It is also considered that P_{CO_2} changes were probably restricted to only 1 order of magnitude. Such changes would not cause substantial deviations of a "steady state" system in equilibrium with silicates and carbonates. Thus the deviations from present value were probably only small ($\sim 8 \pm 1$?).

It is also likely that the average surface temperature in the equatorial belt of the earth did not fluctuate strongly in the geological past. The presence of running water, the continuity of organic life, the presence of ice periods on the one hand and carbonate precipitation on the other even in rocks as old as 2.5-3.4 b.y., and only small change in intensity of solar radiation (Donn et al., 1965; Cloud, 1971; Rutten, 1962; Dunn et al., 1971; Ringwood, 1961; Fairbridge, 1966) all indicate a relatively stable temperature regime for the whole period discussed in this thesis (3.2 b.y.). According to Fairbridge the mean surface temperature of the Earth has probably remained constant within $20 \pm 10^{\circ}C$.

It is obvious that the above model has been selected from conflicting data to build up a consistent hypothesis. It would be possible to devise a model based on a nonequilibrium state of the hydrosphere and atmosphere,

accepting that the ocean is undersaturated with respect to all species, except Ca, and its pH is governed by carbonate-CO_2 equilibria (Ronov, 1968) or some other alternative model. Thus, although I am naturally in favour of the above described model, I realise that the premises are not sufficiently rigorous to exclude alternative hypotheses. Even if true, the model might not be valid for the pre-Archean and possibly even Archean eras of the Earth history. The whole research is still only in its infant stage and therefore is open to criticism.

However, accepting the above discussion, it is possible to predict qualitatively probable changes in the composition of sea water precipitates. Due to the lower P_{O_2} in older periods of the Earth history the Fe, Mn, Mn/Fe and Fe^{2+}/Fe^{3+} should increase with the age. In the silicate buffered hydrosphere the Mg/Ca ratio of sea water should also increase with increasing P_{CO_2}. I am not able to predict the consequences for alkalies, but their association with the detrital fraction of the rocks would probably mask the secondary changes enforced by authigenesis in the ocean and so they may be of lesser interest.

8.1.4 Evolution of the Continental Crust

The last problem to discuss is the influence of changes in average chemical composition of the upper continental crust. The problem is summarised to a considerable degree by Ronov (1964, 1968), Ronov and Yaroshewski (1969), Engel (1963) and others. In general the change from mafic into predominantly sialic composition of the crust should lead to the increased K_2O/Na_2O, CaO/MgO, SiO_2/Al_2O_3 and Fe^{3+}/Fe^{2+} ratios with decreasing age.

The summary of possible changes in chemical composition of sedimentary rocks due to the above discussed factors is presented below (Table 5).

Table 5

Process	Increasing with increasing age	Decreasing with increasing age
(a) diagenetic effects	Al_2O_3, MgO, MgO/CaO, Fe^{2+}/Fe^{3+}, K_2O, K_2O/Na_2O K_2O/Al_2O_3, Rb, Total Fe	CaO, Sr Na_2O, Na_2O/Al_2O_3
(b) evolution of sedimentary environments	MgO, MgO/CaO	CaO
(c) changes in chemical composition of the atmosphere and hydrosphere	MnO, Total Fe, Mn/Fe, Fe^{2+}/Fe^{3+}, MgO, MgO/CaO, SiO_2	(CaO)
(d) changes in chemical composition of the upper continental crust	Na_2O/K_2O, MgO/CaO, Fe^{2+}/Fe^{3+}, Al_2O_3/SiO_2, K/Rb, Sr, Mn, Ti, Mg, Fe Al, Ca, P	K, Na, Si, Rb

As already mentioned and also clearly seen from the table, different effects may lead to the same results. The aim of the following discussion will be to determine the degree to which the apparent geochemical trends with age were caused by different factors.

8.2 SYSTEMATIC DESCRIPTION

8.2.1 Alkalies

The changes in concentrations of alkalies with time are summarized in figs. 23-26. To my knowledge no systematic study of Rb has been published in literature, but the data for Na and K are quite common.

The distributions of K_2O/Al_2O_3, Na_2O/Al_2O_3 and K_2O/Na_2O for Australian carbonates are somewhat different from the trends displayed by sedimentary rocks of the Russian Platform and North America. Whereas the latter indicate

an increase in K/Al for the first 400 m.y. and then gradual decrease, there is no, or only slightly increasing, trend for Australian carbonates. This is in agreement with the data for Australian shales (van Moort, 1971). He observed increasing K content for samples from Tertiary to 2.1 b.y. old. Although he did not analyse the samples for Al_2O_3 and thus it might be claimed that the data may indicate only the decreasing content of carbonates and other soluble phases in shales, it is highly improbable that this explanation might lower the values to such an extent as to be consistent with the other continents. The Australian pattern of Na_2O/Al_2O_3 distribution vs. time is irregular. Excluding the data for Mt. Bruce Supergroup, the ratio is increasing slightly with age and the values are again above the ratios for other continents. The majority of the K_2O/Na_2O values in the present thesis are also above the ratios indicated for other continents. Excluding again the values for Mt. Bruce Supergroup, the shape of the trend in general might be similar to the data for Russian Platform and North America.

Examining first the data for the Russian Platform and North America, it is obvious that there is a reversal of trends in the Late Paleozoic (figs. 23-25). This is clear mainly in the case of K_2O/Na_2O data. The trend for younger periods could be explained by diagenetic factors. The kaolinite-montmorillonite assemblage becomes unstable during deep burial diagenesis and is replaced predominantly by illite. This might account for the increase in K and decrease in Na of the rocks and is supported by the observed loss of K and partly Rb and gain of Na in formation waters of Western Canada during early diagenesis (Billings et al., 1969). Weaver (1967) summarized data for North American shales and noted virtual disappearance of kaolinite and montmorillonite in Mississippian (~340 m.y. ago). He concluded that this was caused by changes in weathering patterns due to the appearance of the land plants. It is however more likely that this is mainly a diagenetic

Figure 23. Variations of K_2O/Al_2O_3 ratios with geological age.
Explanations:
Present thesis: C_{WC} - carbonates of the Western Carpathians, C_A - carbonates of Australia, SRL - Steep Rock Lake Limestones, BL - Bulawayan Limestones. Vertical bars are 1σ limits of the mean.
Ronov and Migdisov (1970, 1971): S_{NA} - sandstones of North America, A_{NA} - Northern American shales and their metamorphosed equivalents, C_{NA} - carbonates of North America, S_{RP} - sandstones of the Russian Platform, A_{RP} - shales and their metamorphosed equivalents from the Russian Platform, C_{RP} - carbonates of the Russian Platform.

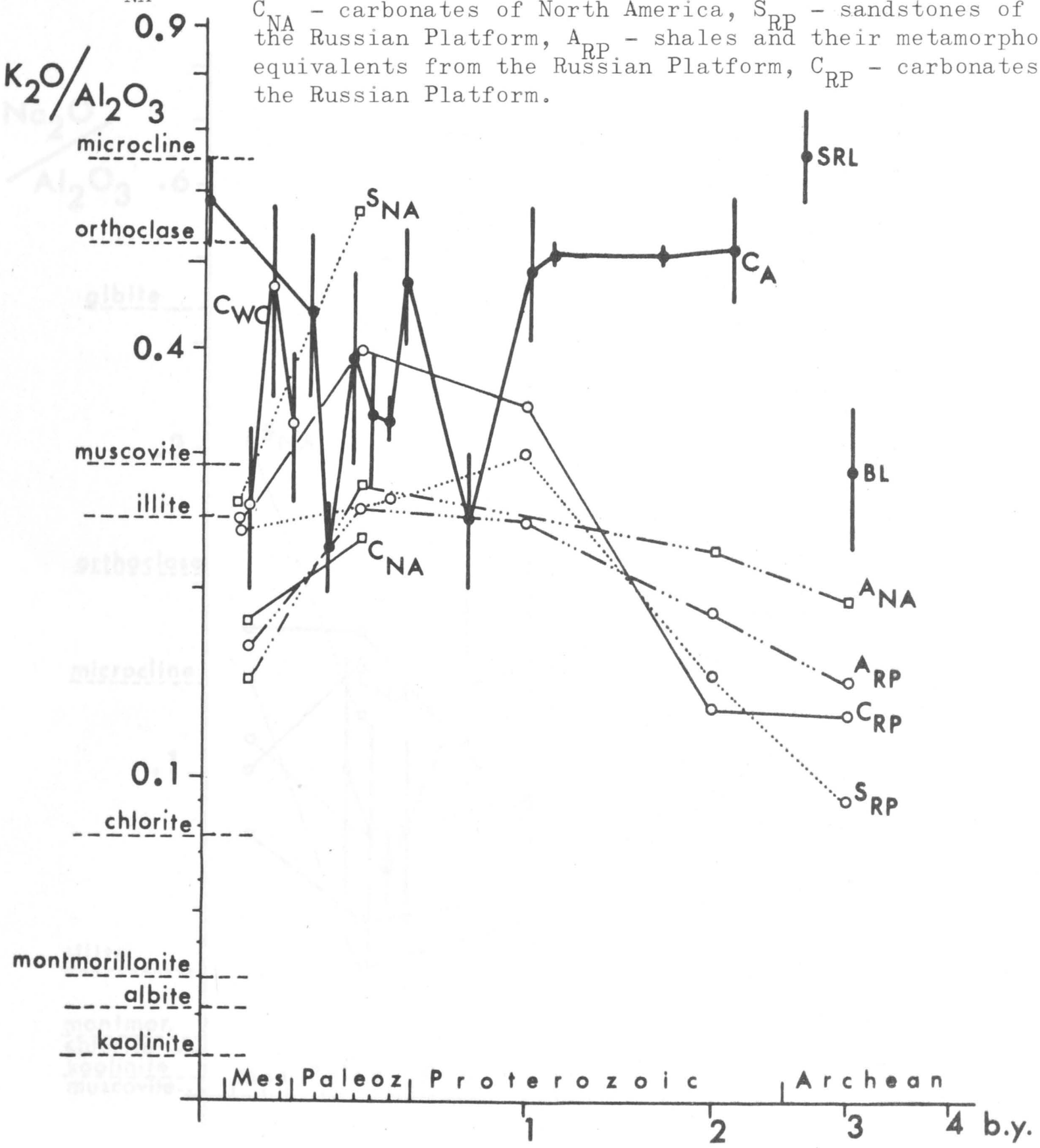


Figure 24. Variations of Na_2O/Al_2O_3 ratios with geological age. Explanations as in figure 23.

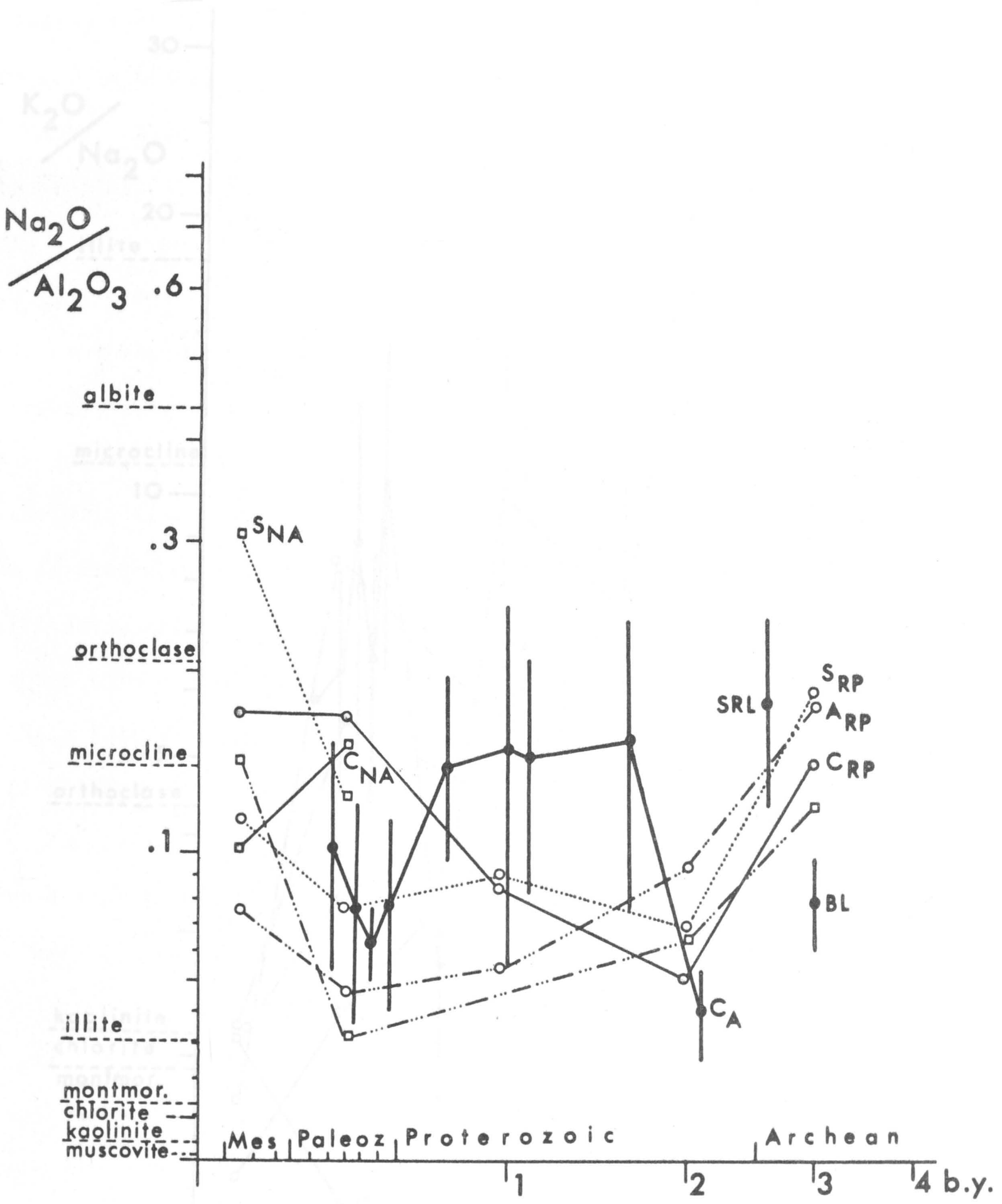
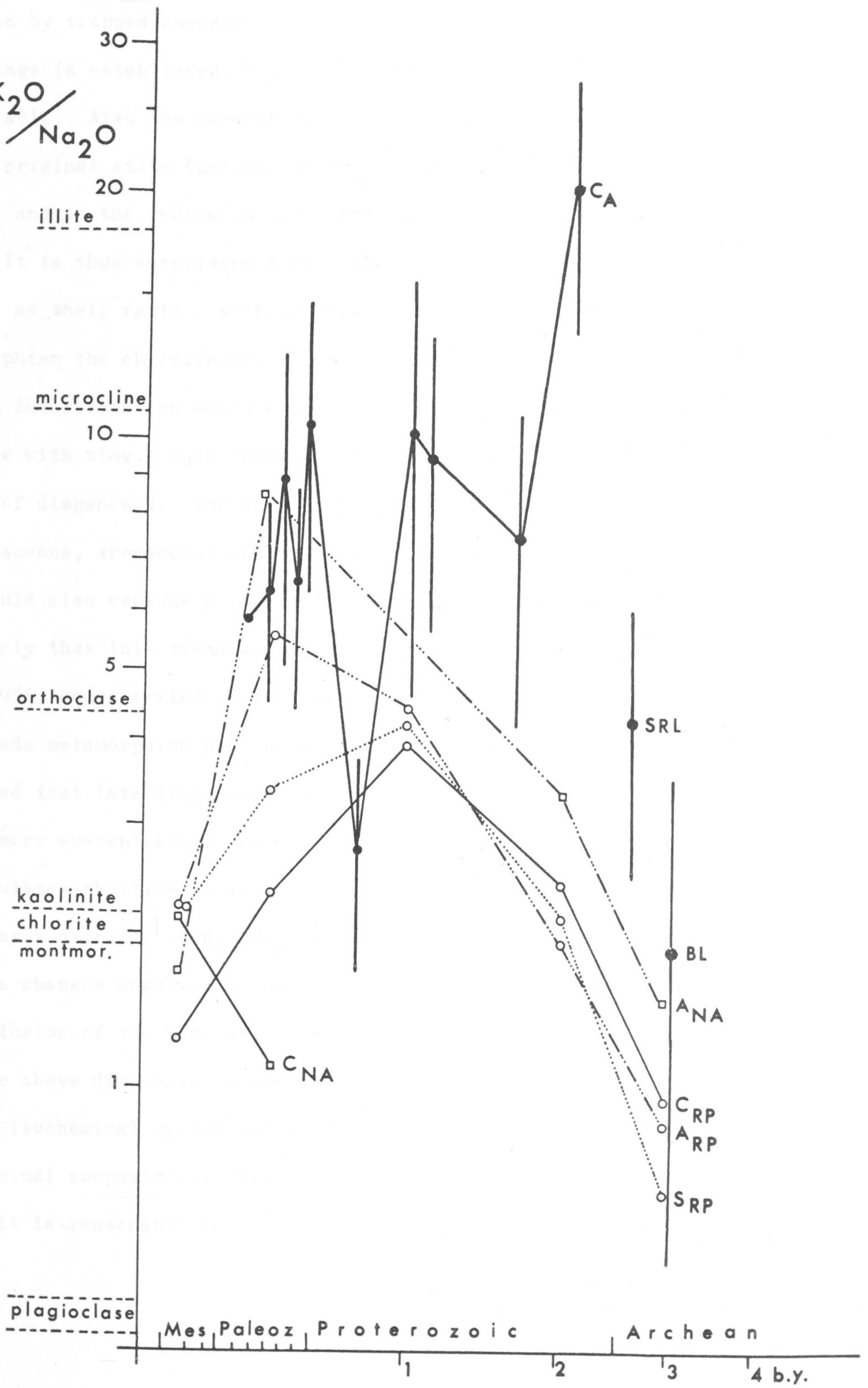


Figure 25. Variations of K_2O/Na_2O ratios with geological age. Explanations as in figure 23.



and/or metamorphic trend as already pointed out by Grim (1953), Siever (1968) and Garrels and MacKenzie (1971a, p. 236). The necessary K could be supplied by trapped connate waters. However, once this stable illitic assemblage is established, the average alkali chemistry should be more or less stable. Also the permeability of rocks at this stage is only a fraction of the original state (porosity $< 3\%$) (Müller, in Füchtbauer and Müller, 1970 p. 246) and so the system should act in the subsequent history as an isochemical unit. It is thus surprising that there is a definite trend for both, K and Na as well as their ratio. With increasing degree of burial diagenesis and/or metamorphism the chlorite-illite assemblage becomes dominant (Müller, 1967). Such an interpretation would not be compatible with the observed Na_2O/Al_2O_3 increase with time. Such chemical adjustment would also require an open system of diagenesis. The existence of similar trends in all types of rocks (argillaceous, arenaceous and carbonates) would not support such an alternative. This would also exclude a possibility of intersediment readjustment. So it is not likely that this trend was caused by diagenesis and/or metamorphism. Shaw (1956) demonstrated statistically, that pelitic rocks of low grade and high grade metamorphism had indistinguishable K_2O and Na_2O contents. It might be argued that late diagenesis is not strictly comparable to metamorphism and is more susceptible to be an open chemical system. For the sequence shales-slates-phyllites-mica schists-kinzingites (Mehnert, 1969, table 9-1), there was a decrease in K_2O/Na_2O ratio by a factor of 2. This is far less than the changes observed in fig. 25 in spite of the much higher p-T range and inclusion of the late diagenetic step within this range.

The above discussion seems to indicate that we are dealing with more or less isochemical system and so the differences in chemistry are reflecting the original composition. Since the trend is evident also within arenaceous rocks, it is reasonable to suppose that the chemical composition was

dominated by a detrital factor and thus reflects the average composition of the source rocks. The easiest way to accommodate the K_2O/Al_2O_3, Na_2O/Al_2O_3 and K_2O/Na_2O trends is to accept that the K-feldspar/plagioclase ratio was decreasing with increasing age of the rocks. This would indicate a higher proportion of mafic rocks in the upper continental crust during early stages of the earth's history. With exception of the diagenetic step this interpretation is similar to the explanation of Ronov and Migdisov (1970, 1971). Certain problems were caused by difficulties in distinguishing between sedimentary and igneous rocks in the Archean and part of the Proterozoic (Ronov and Migdisov, 1970, 1971). Nevertheless this explanation is strongly supported by increasing proportion of graywackes in older sequences (Ronov, 1964). Their later reworking into more mature sediments could be an additional factor increasing K_2O/Na_2O ratio.

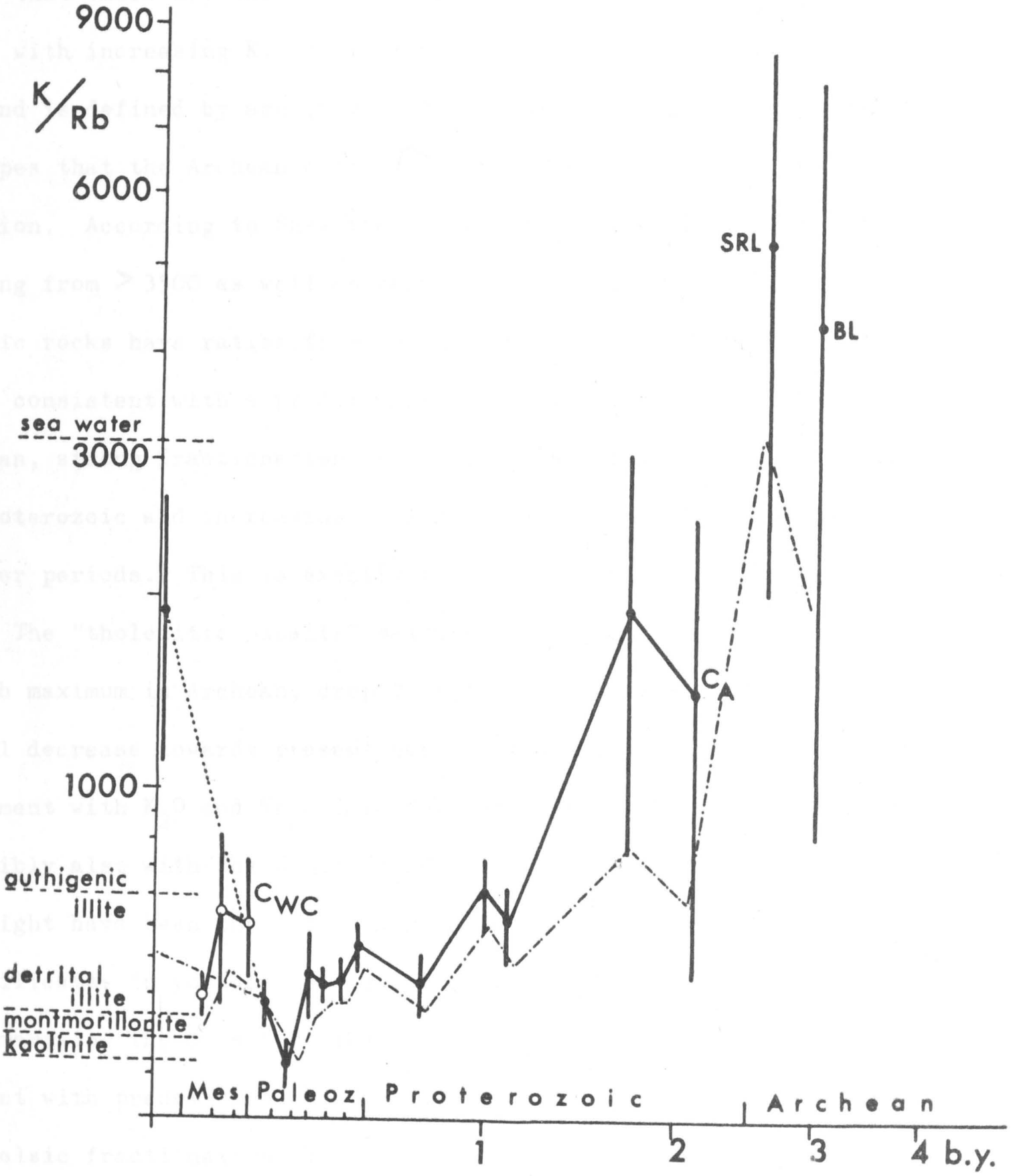
The story may be somewhat different for the mainly Australian data presented here. It was concluded (p. 47) that the high K_2O/Al_2O_3, Na_2O/Al_2O_3 and K_2O/Na_2O ratios in older rocks were probably associated with authigenic minerals (microcline, orthoclase and illite) formed from volcanic tuffs. So the trend for the Australian samples might indicate a less detrital character for the sequences, and may not reflect the source material to such an extent as in the previous cases. The K and Na contents would depend on the initial porosity, mineralogy and composition of the intervening fluid phase. Unfortunately, the scatter of data is too high to advocate any firm conclusion. The Mt. Bruce Supergroup indicates anomalous trends for almost all elements and their ratios, as well as very high scatter in Sr isotopic data. Therefore, if we neglect these samples because their compositions are either anomalous or strongly affected by post-depositional changes, the trends for Na_2O/Al_2O_3 and K_2O/Na_2O become more coherent, and similar to the data from the Russian Platform and the North American sediments. In this case

the conclusion advocated for the latter regions might be at least partly applicable to the Australian and Archean sediments analysed in present thesis. The proportion of "noise" introduced into the present data by other factors, such as diagenesis, cannot be ascertained. The question may be resolved only by accumulation of further data in the future.

The K/Rb ratios might be more sensitive indicators of the chemical composition. It is evident from fig. 26 that the K/Rb ratios increase with increasing age. The high ratios for Recent samples are caused by the presence of sea water salts. The values for Archean and Early Proterozoic are probably too high, because of the extremely low Rb concentrations (below lower detection limit), but the general trend as well as the jump at the Archean-Proterozoic boundary are very likely real. The curve based on the average K/average Rb for each particular sequence (dot-dash line) is much more realistic approximation to the natural situation.

The late diagenesis of clays is dominated by charged net membrane ion filtration and selective membrane filtration (Degens and Chilingar, 1967; Billings et al., 1969 and others). These processes could account for the increase in salinity and chemical changes observed in connate waters. Whether a process such as selective membrane filtration could account for the K, Na and Rb trends observed in present rocks is not clear. According to Billings et al., the rate of K and Rb separation by selective membrane filtration is very slow. In any case, the membrane filtration seems to be more important in the chemistry of connate waters than of shales, and the concentration of these ions in the fluid squeezed out by overburden pressure decreases with increase in pressure (degree of diagenesis). Thus the shales during late diagenesis are acting as more or less closed chemical systems. Therefore even adsorption and cation exchange phenomena might not change the chemistry of the whole rock appreciably. Thus, even if important,

Figure 26. Variations of K/Rb ratios with geological age. Explanations as in figure 23. The dot-dash line is calculated on the basis of the average K/average Rb for the contemporaneous samples.



other factors are probably more decisive in the overall K/Rb evolution. An alternative explanation might be based on the assumption that alkalies for the major part were inherited from source rocks.

Shaw (1968) reviewed K/Rb fractionation trends for igneous rocks. It appeared that there are three fractionation trends in which K/Rb ratios decrease with increasing K. A similar picture is presented in fig. 11 and this trend is defined by age (fig. 26). It will be argued on the basis of Sr isotopes that the Archean continental crust was probably of mafic composition. According to Shaw the oceanic tholeiites have K/Rb ratios decreasing from $>$ 3500 as well as very low K and Rb content. The intermediate and felsic rocks have ratios from about $\sim$400 to $\sim$200. Thus the K/Rb trend might be consistent with a predominantly mafic, little differentiated crust in Archean, strong fractionation of a more felsic crust in Late Archean-Early Proterozoic and increasing felsic/mafic ratio of the continental crust in younger periods. This is exactly the picture presented by Engel et al. (1965). The "tholeiitic basalts" measured on present day continents show very high maximum in Archean, drop in Late Archean-Early Proterozoic and continual decrease towards present period. Thus this explanation would be in agreement with K_2O and Na_2O data for the Russian Platform and North America, and possibly also with the K and Na data in present thesis. An additional factor might have been the decreasing ratio of authigenic/detrital aluminosilicates in younger geological periods.

Summarizing the data for alkalies one may conclude that they would be consistent with predominantly mafic composition of the crust in Archean, strong felsic fractionation phase in Late Archean-Early Proterozoic and increasing proportion of felsic constituents in younger periods. The data, to some degree, also indicate increased reworking and maturity, decreased proportions of authigenic aluminosilicates, and less diagenetic alteration

in younger sedimentary rocks.

8.2.2 Iron and Manganese

It was shown in figs. 21 and 22, that both Mn and Fe increase markedly with increasing age of the rocks. When Fe and Mn are normalised to Al_2O_3 in order to exclude the scatter caused by variations in aluminosilicate content, the increasing trends are observed for the majority of lithologies and continents (fig. 27). The increase for detrital rocks is however very small or nonexistent and this indicates that the excess Fe and Mn is present mainly in the form of carbonates. As noted previously (fig. 13) carbonates of humid periods contain higher Mn and Fe concentrations. Comparing fig. 1 with figs. 27-29, it is evident that for post-Cambrian history this is indeed the case. Quaternary, Triassic, Devonian and Ordovician (arid) contain lower concentrations than Cretaceous, Jurassic, Permian, Carboniferous and Silurian (Humid). Since the majority of older periods were probably characterised by arid climates, they should be compared only with the arid periods of the post-Cambrian history. This would make the Fe and Mn increases in older rocks even more pronounced.

These increases may be partly due to the greater proportion of the early diagenetic dolomites in older sequences and could perhaps be attributed to the ease of Fe and Mn substitution for Mg. However, the trends are obvious even when rocks of similar lithologies are compared, e.g. early diagenetic dolomites. It is also unlikely that this increase could be explained by diagenetic factors only. Although alteration of carbonate rocks by continental waters during diagenesis could lead to ankerite and siderite formation (Curtis, 1967), this might not explain the magnitude of changes. The presence of widespread banded iron ore formations in the early Precambrian and their virtual absence in younger geological periods (James, 1954, 1966; Lepp and Goldich, 1964; Ronov, 1964 and many others) indicates that this

Figure 27. Variations of total Fe/Al_2O_3 ratios with geological age. Explanations as in figure 23.

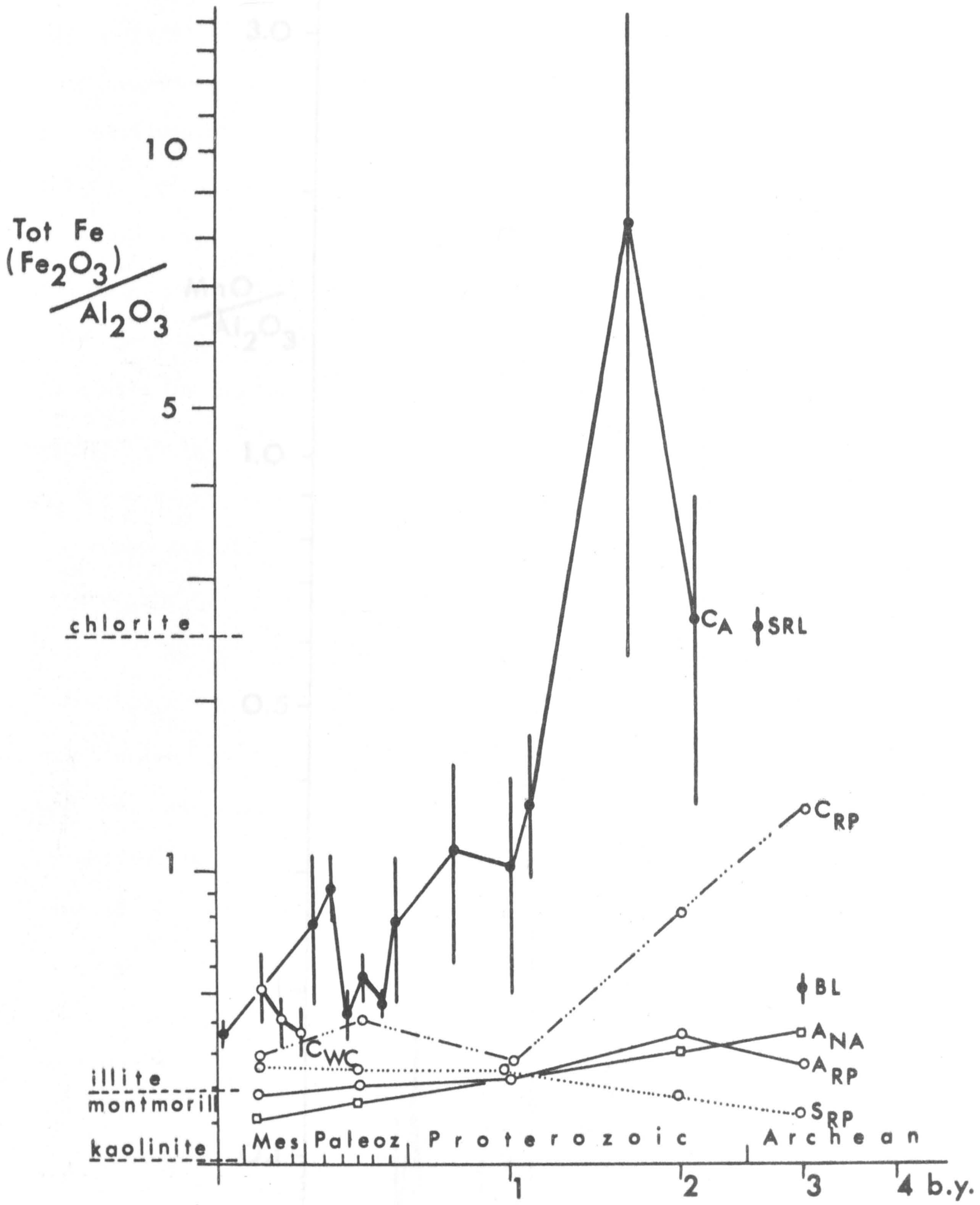
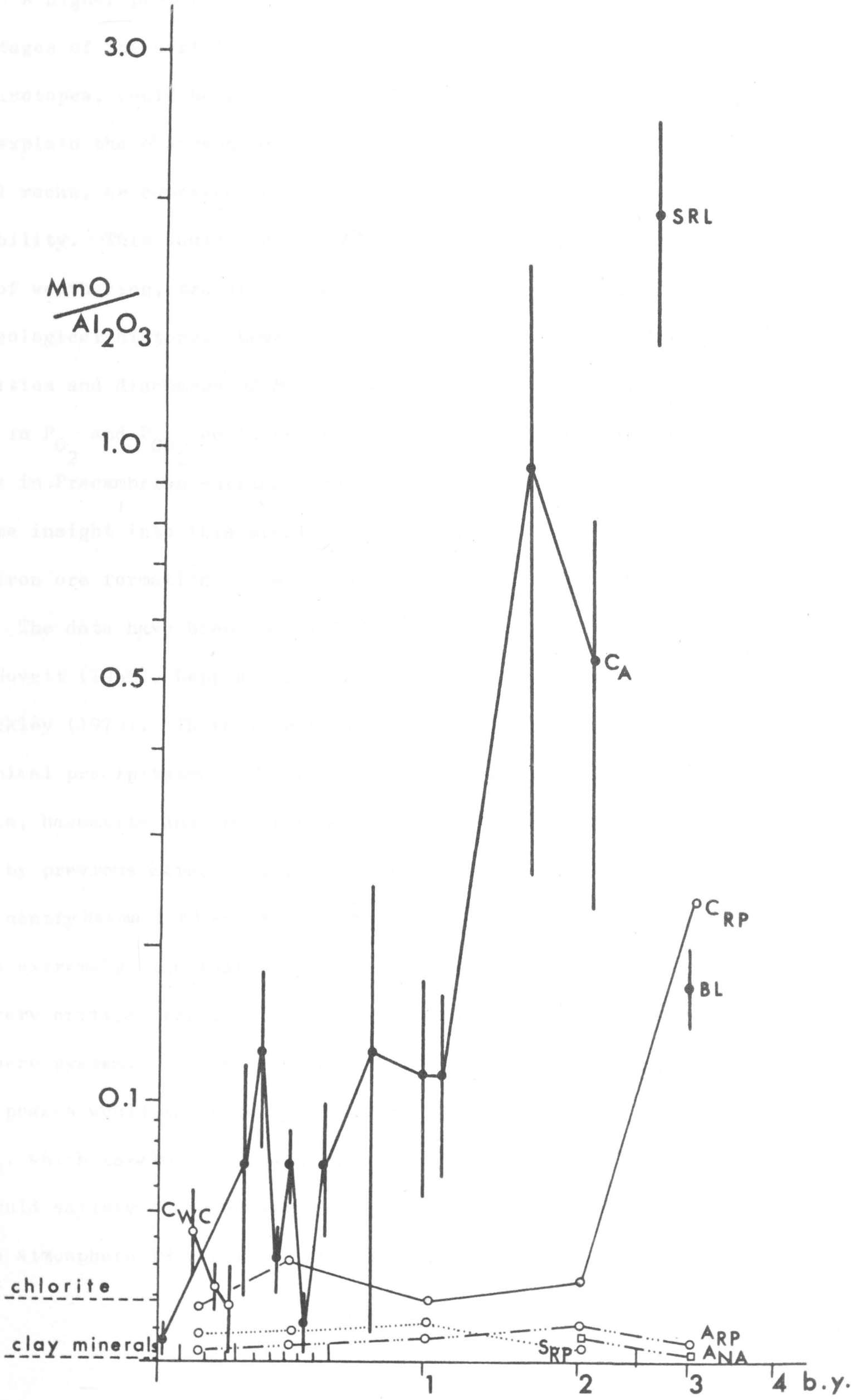


Figure 28. Variations of MnO/Al_2O_3 ratios with geological age. Explanations as in figure 23.



feature is of general importance and cannot be attributed to any secondary factor. A higher proportion of mafic rocks in the continental crust during early stages of the earth's history, as advocated on the basis of alkalies and Sr isotopes, could be a source of higher supply of Fe and Mn, but again cannot explain the observed magnitude of changes. The small change for detrital rocks, as compared to carbonates, argues decisively against such a possibility. This would indicate that we are dealing with a different system of weathering, transport and precipitation of Fe and Mn in progressively older geological history. Lower pH and Eh of surface waters lead to higher solubilities and discharge of Mn and Fe into marginal sea basins. Thus changes in P_{O_2} and P_{CO_2} could be the cause of higher concentrations of those elements in Precambrian surface waters and oceans.

Some insight into this problem could be gained from consideration of banded iron ore formations. Detailed discussion is outside the scope of this thesis. The data have been summarised by many authors, e.g. James (1954, 1966), Govett (1966), Lepp and Goldich (1964) and for Australia by Trendall and Blockley (1970). There is general agreement that the banded iron ores are chemical precipitates. Their mineralogy is predominantly siderite, magnetite, haematite and less pyrite and Fe silicates. The question strongly debated by previous authors is the primary or secondary origin of Fe oxides (predominantly haematite) and Fe silicates. Since the stability field of Fe_2O_3 is extremely wide (Garrels and Christ, 1965, p. 144), the discussion is not very critical for interpretation of higher P_{O_2} in the atmosphere-hydrosphere system. The presence of the above assemblage as original mineral phases would indicate P_{O_2} values close to the lower stability limit of Fe_2O_3, which is $\sim 10^{-70}$. Eh-pH in present day natural aqueous systems, which would satisfy those conditions, are typical for environments isolated from the atmosphere (Garrels and Christ, 1965 p. 381). For the range of pH

common in surface waters (5-9) the Eh would be ≤0. Unfortunately the solubility of O_2 in H_2O is strongly dependent on a number of physico-chemical and biological variables. Thus the oxidation state of a particular water body is determined by a sequence of redox reactions which are generally biologically mediated (Baas Becking et al., 1960). This sequence for present sea water (pH = 8.1 and atm. P_{O_2} = 0.21 atm.) was summarised by the "titration curve" of Sillén (in Stumm and Morgan, 1970 p. 338). If the Eh values of aquatic media during the deposition of banded iron ore formations were close to the Fe_2O_3-Fe_3O_4 ($FeCO_3$) boundary, or slightly higher for well aerated waters, it may indicate a deficiency of O_2 in the contemporaneous atmosphere. Although, due to the problems caused by stratification of water, depth of the basin, organic life, temperature, circulation etc., such a conclusion cannot be advocated unequivocally, it is highly probable. It seems to be supported by other geological criteria as summarised by Rutten (1962, 1966), but the presence of red beds advocated as an indicator of high atmospheric P_{O_2} is of little diagnostic value.

Accepting that the P_{O_2} in early geologic history was indeed lower than at present, the increasing Mn and Fe content should be expected (cf. p. 69). According to Krauskopf (1967 p. 82) observed concentrations of $MnCO_3$ and $FeCO_3$ in sea water were 4×10^{-8} and 2×10^{-7} moles liter^{-1}. The theoretical concentrations could be 1.5×10^{-4} and 8×10^{-5}. This discrepancy is apparently due mainly to the strong oxidation of Fe and Mn and their precipitation as oxides. Thus the concentrations of Mn and Fe could increase considerably by decrease of P_{O_2} only. This could possibly account for the increase in Mn and Fe phases in ancient rocks. Continental surface waters could also carry much higher loads of those elements. If this is coupled with increase in P_{CO_2} by factor of 5-10 (p. 64) the resulting lower pH and Eh of continental waters would result in higher rate of weathering and

transport of Fe and Mn in solution into the sea. According to Hem and Croper (1959, in Joliffe, 1966) the solubility of Fe at pH = 6 and Eh = 0 would be about 10^4 times higher than at present. From this discussion it seems probable that the increase in Mn and Fe content of older rocks could be explained mainly by changes in the P_{O_2} and P_{CO_2} and to a lesser degree by additional factors, such as composition of the source rocks and diagenesis.

It was discussed previously (p. 53) that the separation of Fe from Mn, as well as the higher increase in solubility of Mn compared to Fe, were dependent on P_{O_2}. Thus with decreasing P_{O_2} the Mn/Fe ratio should increase. For rocks studied during this project the trend is quite clear from fig. 29, although the scatter is high. This scatter in post-Cambrian history could be explained by climatic factors, with higher Mn/Fe ratios during humid periods. The data for other continents are inconclusive, except for iron ores discussed by Lepp and Goldich (1964). The increase for shales from the Russian Platform presented by Ronov and Migdisov (1970, 1971) is very small compared to carbonates in my data and there is also a reverse of sign in Archean. This again points out that the increase in Mn/Fe ratio with age is not an inherited detrital feature, but reflects the chemistry of aqueous solutions.

Another possible test of the oxidation state in sedimentary environments would be to compare the Fe^{2+}/Fe^{3+} ratios of rocks. The increasing reduction state with increasing age is quite clear for all lithologies as well as continents (fig. 30) (Nanz, 1953; Ronov, 1964; Ronov and Migdisov, 1970, 1971; Rankama, 1955; Engel, 1963; Lepp and Goldich, 1964; Kazakov, 1967). It is well known that increasing diagenesis and/or metamorphism would increase Fe^{2+}/Fe^{3+} ratios (Miyashiro, 1964; Shaw, 1956; Ronov and Migdisov, 1970, 1971 and others). The change in Fe^{2+}/Fe^{3+} ratio over the whole range from shales to kinzingites (table 9-1 in Mehnert, 1969) is by a factor of 3.4.

Figure 29. Variations of MnO/Total Fe ratios with geological age. Explanations as in figure 23. FE_{NA} - iron ores of North America (Lepp and Goldich, 1964).

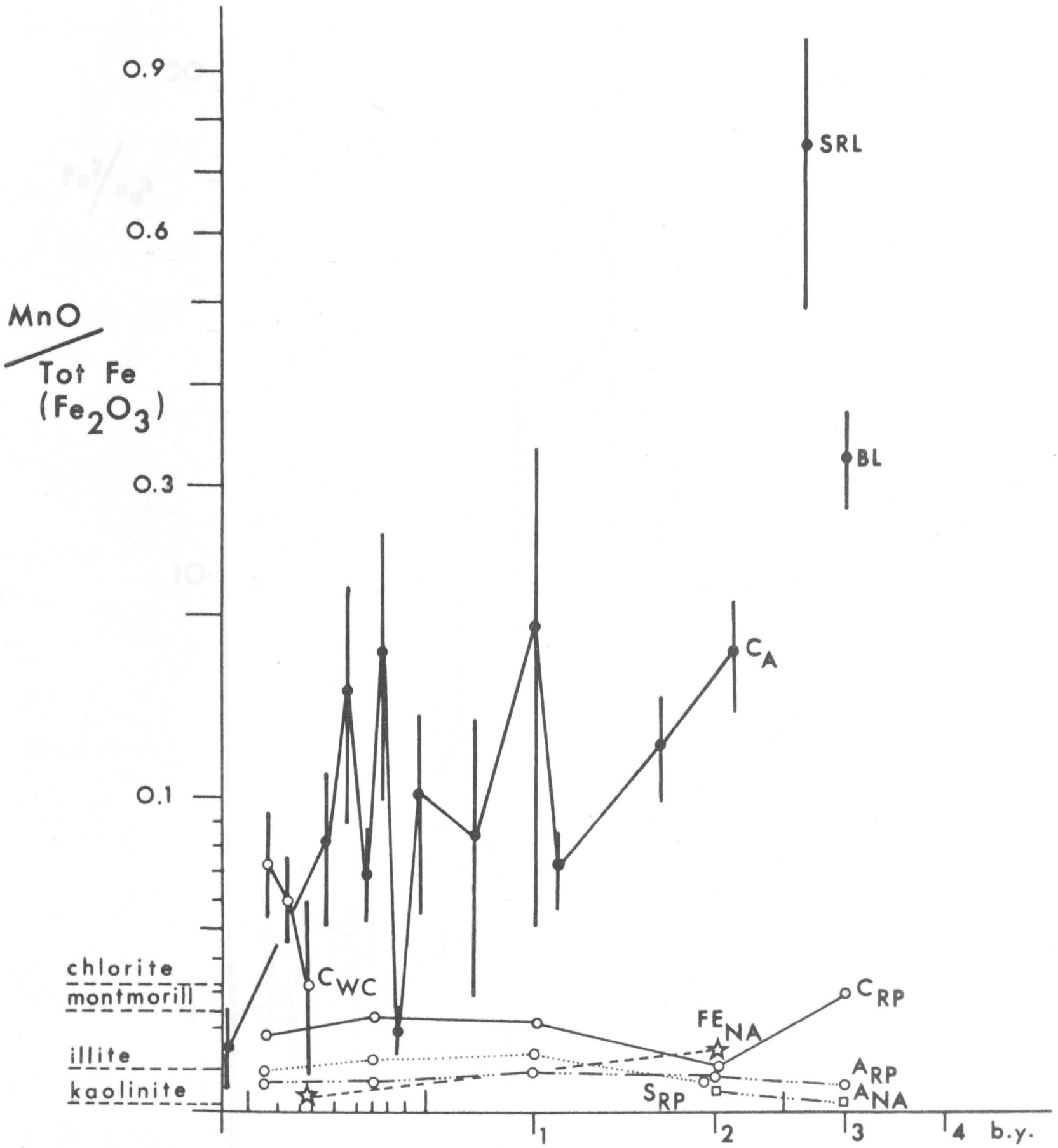
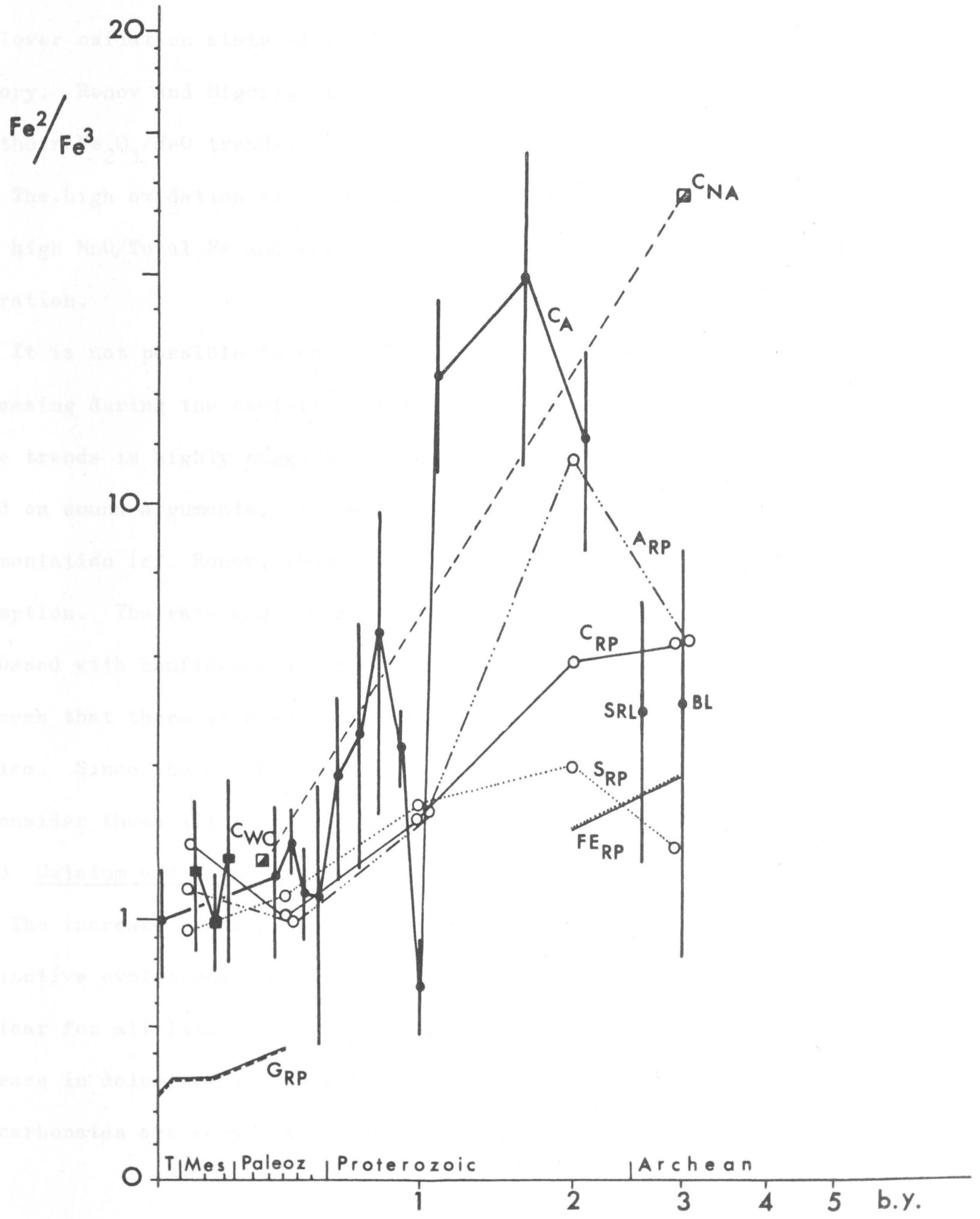


Figure 30. Variations of Fe^{++}/Fe^{+++} ratios with geological age. Explanations as in figure 23. FE_{RP} - iron ores of the Russian Platform (Ronov and Migdisov, 1970, 1971), G_{RP} - glauconites of the Russian Platform (Kazakov, 1967).



This indicates that a substantial part of the increase could be attributed to diagenetic factors, although it is not possible to equate strictly diagenesis and metamorphism. The strongest reducing agent during diagenesis is organic matter. Since the positive correlation of organic matter (or C) with Fe^{2+}/Fe^{3+} was very poor and the early diagenetic dolomites were probably low in organic content, at least part of the increase could be attributed to the lower oxidation state of sedimentary environments during early geologic history. Ronov and Migdisov (1970, 1971) advocated a similar explanation for their Fe_2O_3/FeO trends.

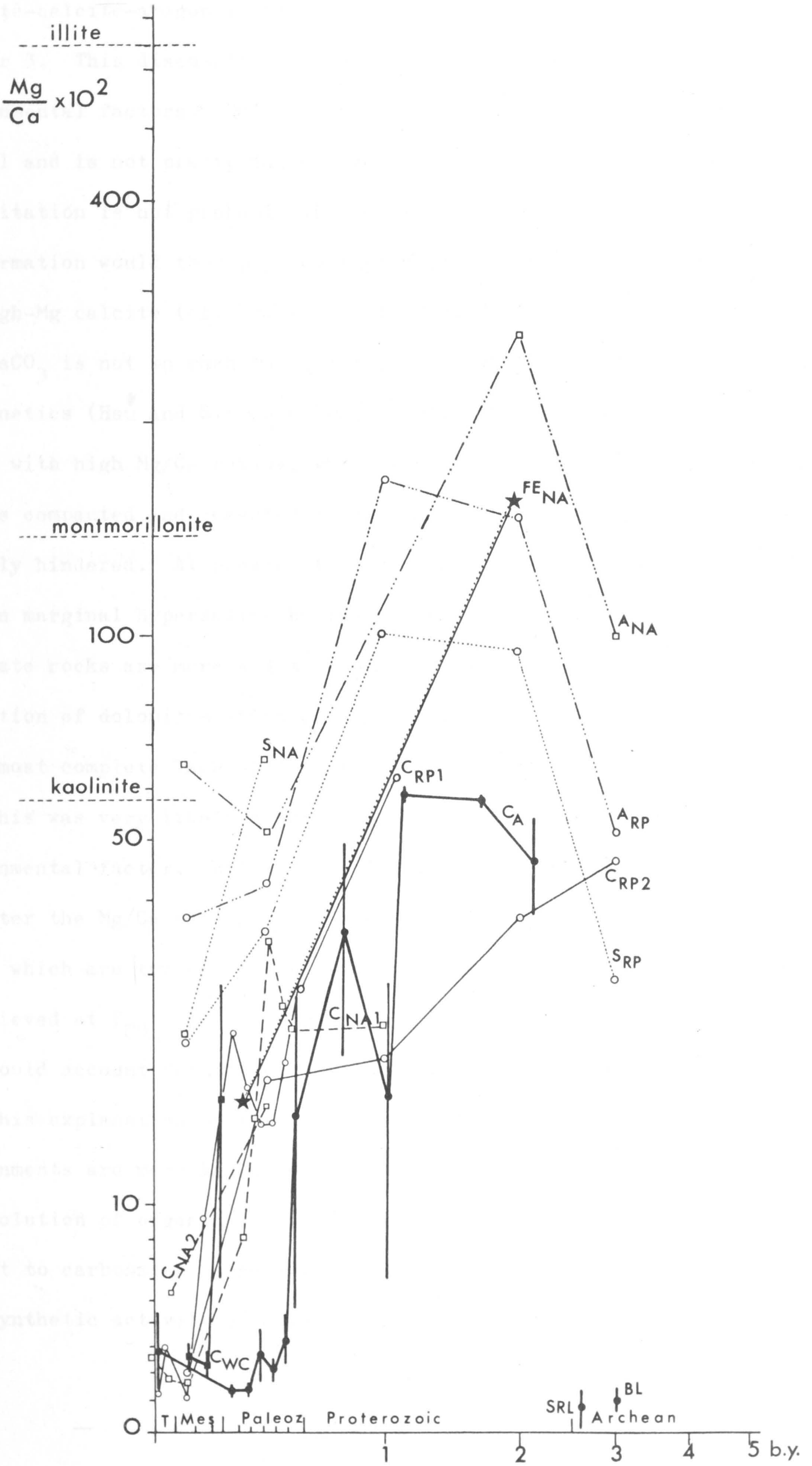
The high oxidation state of the Bitter Springs Formation, together with very high MnO/Total Fe and very low Sr, suggests to me a strong postdepositional alteration.

It is not possible to conclude with certainty that the P_{O_2} was increasing during the evolution of the Earth, but the consistency of the above trends is highly suggestive. Therefore the hypothesis seems to be based on sound arguments. The evolution of chemical and biochemical sedimentation (cf. Ronov, 1964) could be also consistent with such an assumption. The rate and timing of these evolutionary changes cannot be discussed with confidence at the present stage. From the geological record it seems that there were several periods which might be related to this problem. Since the O_2-CO_2 cycles are complementary, it is more convenient to consider these after discussion of the Mg/Ca trends (Chapter 12).

8.2.3 Calcium and Magnesium

The increase in Mg/Ca ratio with increasing age is probably the most distinctive evolutionary feature of sedimentary rocks (fig. 31). This trend is clear for all lithologies and continents and is probably related to the increase in dolomite/calcite ratio. Higher values for detrital rocks than for carbonates are very likely caused by additional Mg associated with

Figure 31. Variations of (Mg/Ca) x 10^2 ratios with geological age. Explanations: C_{NC}, C_A, SRL, BL, S_{NA}, A_{NA}, S_{RP} and A_{RP} as in figure 23. C_{RP_1} - carbonates of the Russian Platform (Vinogradov et al., 1952), C_{RP_2} - carbonates of the Russian Platform (Ronov and Migdisov, 1970, 1971), C_{NA_1} - carbonates of North America (Daly, 1909), C_{NA_2} - carbonates of North America (Ronov and Migdisov, 1970, 1971), FE_{NA} - iron ores of North America (Lepp and Goldich, 1964).


illite
Mg/Ca x10²
400
montmorillonite
100
kaolinite
50
10
0
FE NA
A NA
S NA
C RP1
C A
A RP
C RP2
S RP
C NA1
C NA2
C WC
T
Mes
Paleoz
Proterozoic
SRL
BL
Archean
1
2
3
4
5 b.y.

aluminosilicates. Thus the discussion could be limited basically to the dolomite-calcite-aragonite minerals. The problem was partly considered in Chapter 3. This discussion suggests that this trend was caused by environmental factors. Dolomite at present is very likely only a diagenetic mineral and is not precipitated directly from sea water. Its direct precipitation is not probable in view of its highly ordered structure and its formation would thus proceed through metastable phases such as aragonite and high-Mg calcite (cf. Krauskopf, 1967 p. 85). The formation of dolomite from $CaCO_3$ is not so much the question of stability as of Mg availability and kinetics (Hsü and Siegenthaler, 1969). The transformation requires brines with high Mg/Ca ratios, which would cause this alteration before the rock is compacted and cemented to such a degree that further conversion is strongly hindered. At present the solutions of such composition are formed only in marginal hypersaline basins. Since the sedimentary environments of carbonate rocks are more and more restricted in older periods, the higher proportion of dolomites would be compatible with such an interpretation. The almost complete lack of limestones in sequences 1-2 b.y. old indicates that this was very likely a more general phenomenon than implied by the environmental factor. Holland (1965) showed that in the silicate buffered sea water the Mg/Ca ratio would increase with increasing P_{CO_2}. The $^{m}Mg/^{m}Ca$ values which are typical for present day dolomite environments ($\sim$20) would be achieved at P_{CO_2} $10^{-2.9}$ (Stumm and Morgan, 1970). Thus the increasing P_{CO_2} could account for the higher dolomite/limestone ratio.

This explanation by itself would not however explain why the sedimentary environments are more and more restricted. The obvious answer seems to be the evolution of organic life. Since the inorganic supersaturation with respect to carbonates is achieved mainly in shallow warm seas (aided also by photosynthetic activity of algae) the restriction to such basins is not

surprising. The evolution of higher organic life probably explains the formation of carbonate shells and the migration of the carbonates into neritic and pelagic environments. The above explanation superficially seems to be quite satisfactory.

On the other hand, it is noted that organic processes are in general only speading reactions which would proceed anyhow inorganically (Krauskopf, 1967; Stumm and Morgan, 1970). Their presence serves only as catalyst. If this argument is accepted, one is forced to postulate that the formation of organic skeletons would follow inorganic saturation.

In a silicate + carbonate buffered ocean the increasing P_{CO_2} would cause several effects. It would decrease solubility of Ca and so increase Mg/Ca of sea water as already discussed. Müller et al. (1971) observed that aragonite is precipitated in environments with $^{m}Mg/^{m}Ca$ ratio >25, high-Mg calcite and/or aragonite in the range 1-25 and low-Mg calcite <1. In sea water with $^{m}Mg/^{m}Ca$ ratio ~ 20 the precipitated phases would be the metastable aragonite and/or high-Mg calcite. Supersaturation with respect to those species would be approached mainly in semi-restricted warm shallow basins, and the precipitates would be quickly altered to dolomite during early diagenesis. The original aragonitic nature of such sediments was advocated on the basis of Sr concentrations by Veizer (1970a).

Higher P_{CO_2} might also shift the carbonate compensation line upward. Thus even if supersaturation with respect to aragonite or high-Mg calcite was achieved in pre-Jurassic times at the surface of the open sea, the precipitated metastable phases would be quickly redissolved at very shallow depth. The dissolution would be aided also by much smaller grain size of inorganic precipitates and the precipitation as such would be hindered by the lack of nucleation centers which are provided by organic activity. There is no general agreement as to the depth of the carbonate saturation

level at present. Li et al. (1969) claim supersaturation for calcite to the depth of 500 m in the Pacific and 4000 m in the N. Atlantic, whereas Berner (1965) argues that both oceans are undersaturated below the depth of 500 m. Similarly Pytkowicz (1965) indicates undersaturation for the SE Pacific below 100 m. The estimates for aragonite and high-Mg calcite would be proportionally lower (200 and 1000 m for aragonite by Li et al.).

Only after the drop in Mg/Ca ratio of sea water to approximately its present value, which enabled the (organic?) precipitation of the relatively stable low-Mg calcite, could the accumulation of $CaCO_3$ proceed in the deeper neritic and pelagic environments. Chilingar and Bissel (1963) also argued that the high Mg/Ca of the Precambrian oceans might cause the lack of calcareous skeletons in the sediments of this era.

The role of stability and solubility of carbonate minerals might be in accord with the observation that many of the early organisms inhabiting the new environments seem to have had low-Mg calcite skeletons. Thus the shells of coccoliths and pelagic foraminifera are formed by low-Mg calcite. The aragonitic pteropods are only very small part of deep sea carbonate sediments. It seems also that all the important Cambrian groups, i.e. trilobites, brachiopods and possibly also Archaeocyatha were formed by low-Mg calcite (cf. Füchtbauer, in Füchtbauer and Müller, 1970 p. 290 and this thesis p. 98). It is also noteworthy that the proportion of Ca-phosphate skeletons among Cambrian and Ordovician organisms is much higher than that in younger periods (Rutten, 1962 and Müller, 1964). Apatite is not only more stable than $CaCO_3$, but it generally slightly preceeds the precipitation of $CaCO_3$ on the open shelf areas (Krauskopf, 1967 p. 88).

The above discussion might indicate that changes in P_{CO_2} could be the controlling factor in the carbonate mineralogy, although this control might not be exercised directly. Since any further discussion of the subject is

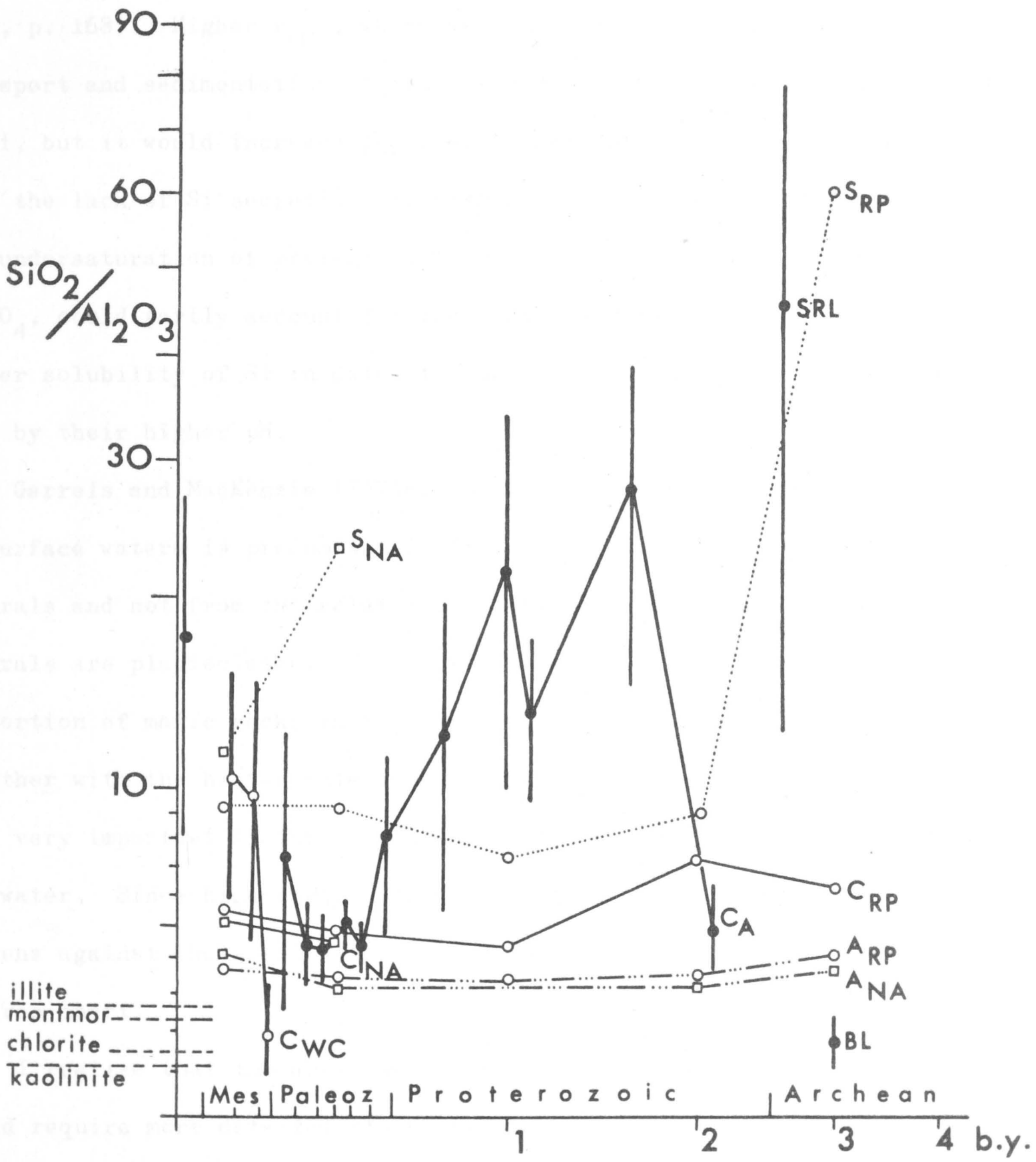
very speculative and related to other speculative subjects, it is better to discuss them together in one chapter (Chapter 12).

8.2.4 Silica and Aluminium

From fig. 32 it seems apparent that SiO_2/Al_2O_3 ratio shows a general increase with age. This is particularly clear for the Australian carbonates. With the exception of the oldest Mt. Bruce Supergroup, and the Recent sample No. 2, in which the high ratio is caused by detrital quartz, the increasing trend is quite obvious. Following the discussion on p. 44, one might conclude that this trend was caused by increasing content of early diagenetic dolomites and chalcedony associated with it and thus is caused by environmental factors. Although this is undoubtly a very important phenomenon, the full story is probably more complicated.

Similar trends with much shallower slope were observed by Ronov and Migdisov (1970, 1971) for the Russian Platform and the North American shales and their metamorphosed equivalents. Since the detrital sediments generally reflect compositions of the source rocks, the decreasing SiO_2/Al_2O_3 ratio towards younger periods is surprising. That the evolution of the continental crust proceeded from mafic to a more sialic one is clearly indicated by Al_2O_3/SiO_2 modulus for the whole crust (Ronov and Yaroshewski, 1969), as well as for both platforms (Ronov and Migdisov, 1970, 1971). Consequently one would expect the trend for shales to be of opposite sign. To explain this anomaly Ronov and Migdisov concluded that the original sediments were polymictic immature rocks (graywackes and arkoses) formed by weathering of the contemporaneous crust and this could account for the relatively high SiO_2 content. With increasing degree of reworking they were separated into clays and sandstones and thus SiO_2/Al_2O_3 ratio of argillaceous rocks decreased with time. This explanation is supported by the decreasing importance of polymictic detrital rocks and increasing proportion of mature

Figure 32. Variations of SiO_2/Al_2O_3 ratios with geological age. Explanations as in figure 23.



sediments towards younger geological periods (Ronov, 1964; Cloud, 1969).

This explanation is hardly valid for carbonate rocks incorporated in fig. 32. The presence of excess Si mainly as chalcedony indicates that we are dealing with true solutions or colloids. This may be supported by the well known alternation of iron and chert layers in the banded iron ore formations. Dissolution of Si is independent of pH at values < 9 (Krauskopf, 1967, p. 168). Higher P_{CO_2}, which was invoked to explain the weathering, transport and sedimentation of iron, would not thus influence the solubility of Si, but it would increase the overall rate of weathering. This, together with the lack of Si secreting organisms, which are probably responsible for the undersaturation of present surface and ocean waters with respect to H_4SiO_4, could partly account for the higher dissolved Si in older periods. Higher solubility of Si in dolomitic sedimentary environments might be aided also by their higher pH.

Garrels and MacKenzie (1971a, chapter 6) clearly documented that H_4SiO_4 in surface waters is predominantly from incongruent solution of silicate minerals and not from the relatively stable quartz. The most susceptible minerals are plagioclases. The lack of mature sediments and the higher proportion of mafic rocks in the early stages of the earth's history, together with the higher rate of weathering caused by increased P_{CO_2} could be a very important factor responsible for the high H_4SiO_4 of contemporaneous sea water. Since higher P_{CO_2} would also stabilize carbonates of divalent cations against their silicates, the high H_4SiO_4 will be precipitated mainly as free chert.

I realise that the above explanation is not entirely satisfactory and would require more detailed study in future. The explanation also does not account for such structural features as banding of iron ore formations and other phenomena, but it is the best explanation I am able to produce at present stage.

8.2.5 Titanium and Phosphorus

There is no trend, or only a slightly decreasing one, in TiO_2/Al_2O_3 ratios with age.

There is no trend for P_2O_5/Al_2O_3 ratios with age. The scatter of data is very high. There are extremely high ratios in the Archean samples and in the Carboniferous and Permian brachiopods. The latter could be attributed to the presence of apatite in their skeletons (Lowenstam, 1963; Wolf et al., 1967).

Chapter 9

STRONTIUM

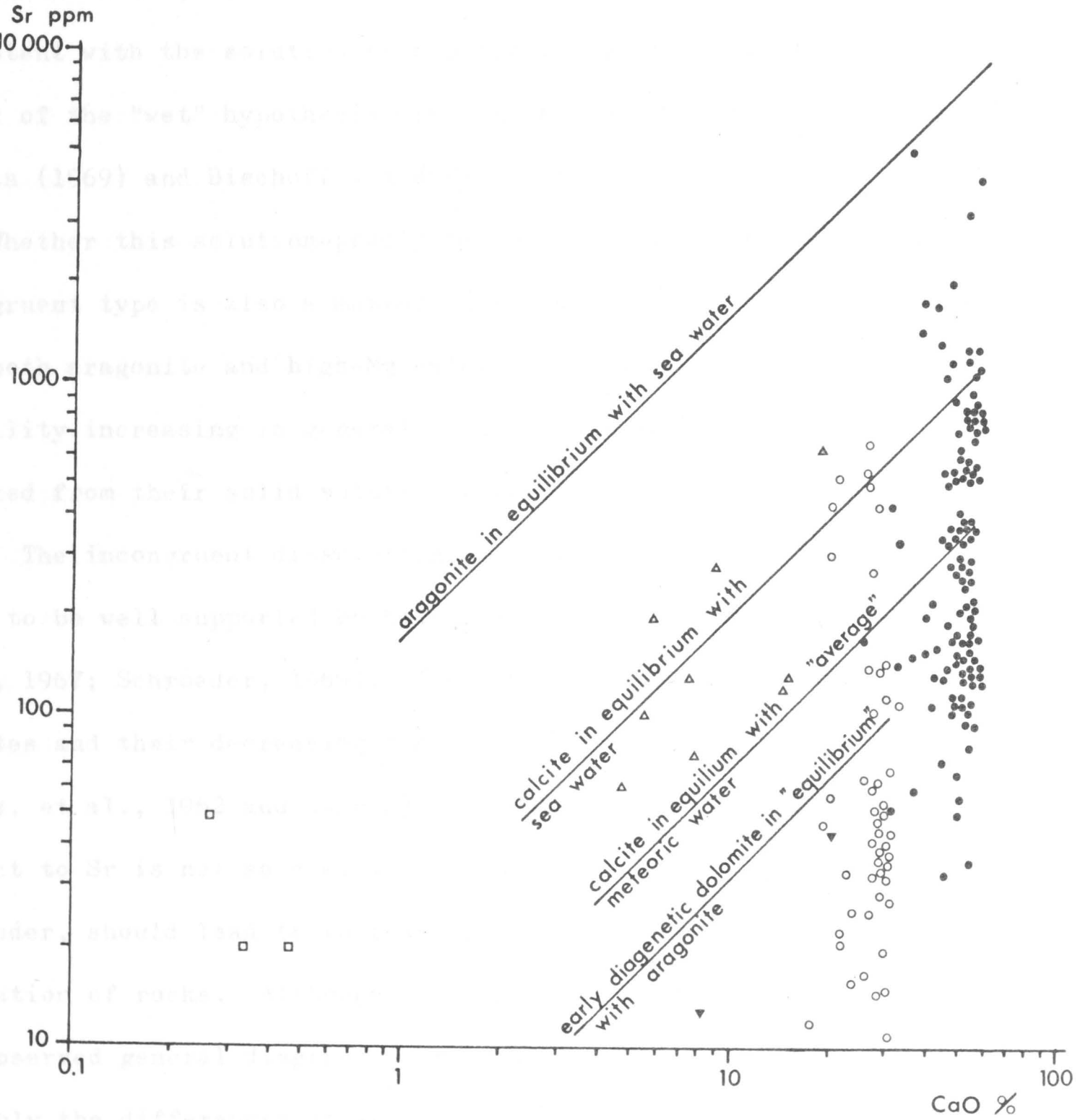
For the whole group of carbonate rocks the linear correlation coefficient of Sr is statistically significant only with CaO (Table 3). The small value of the correlation coefficient (fig. 33) is almost certainly caused by a diagenetic effect, which will be discussed later. In fact Sr is the most important minor element of carbonate rocks (cf. Kinsman, 1969; Wolf et al., 1967; Graf, 1960 and others), although its correlation with CaO is far from being linear. Strontium substitutes for Ca in lattices of carbonate minerals, Ca sulphates and is also present as $SrCO_3$ (strontianite) and $SrSO_4$ (celestite) in some "evaporitic" sequences.

9.1 DIAGENETIC BEHAVIOUR

For the understanding of the geochemistry of strontium, it is relevant to discuss shortly the mineralogy of recent and fossil carbonate sediments.

Recent carbonate sediments are formed almost exclusively by high-Mg calcite, low-Mg calcite and aragonite (Winland, 1969; Taft, 1967; Friedman and Sanders, 1967). Other metastable minerals and dolomite are volumetrically not important. Fossil sediments, on the other hand, are formed by low-Mg calcite and dolomite (cf. Chilingar et al., 1967 and others). It is thus obvious that the diagenetic changes producing lithified rocks are limited basically to the conversion of metastable high-Mg calcite and aragonite into low-Mg calcite and dolomite. The general diagenetic stability is increasing (solubility decreasing) in the order high-Mg calcite $\leqslant$ aragonite $<$ low-Mg calcite $<$ dolomite (Bricker and Garrels, 1967, in Stumm and Morgan, 1970, p. 211).

Figure 33. Scatter diagram of Sr vs. Cao.
Explanations as in figure 5.



The problem in understanding the diagenesis, is not the general succession of mineral phases, but the way in which these changes are achieved. Because of the well known preservation of organic structures, it was widely assumed that the above inversion in mineralogy was of a "solid-solid" nature. Although, given a critical activation energy (about 250 cal/mol for aragonite (Latimer, 1959), not known for high-Mg calcite), the "dry" transformation would be possible (cf. Kunzler and Goodel, 1970; Fyfe and Bischoff, 1965 and others), the geological occurrences are more consistent with the solution-precipitation hypothesis. The arguments in favour of the "wet" hypothesis are summarised by Goodel and Garman (1969), Kinsman (1969) and Bischoff and Fyfe (1968).

Whether this solution-precipitation process is of a congruent or incongruent type is also a matter of dispute. Schroeder (1969) maintains that both aragonite and high-Mg calcite are dissolved incongruently; the solubility increasing in general in the order Mg > Ca > Sr. This would be expected from their solid solution properties (Stumm and Morgan, 1970, p. 209). The incongruent dissolution of Mg ($MgCO_3$) from metastable minerals seems to be well supported by both field evidence and experimental data (Land, 1967; Schroeder, 1969). The generally low stability of high-Mg calcites and their decreasing content during diagenesis is well known (Chave, et al., 1962 and others). The incongruent dissolution of Ca with respect to Sr is not so clear. The lower solubility of Sr as claimed by Schroeder, should lead to increasing Sr/Ca ratios with increasing diagenetic alteration of rocks. Although he is quoting several examples of such trends, the observed general diagenetic trend is of the opposite sign (see fig. 35). Possibly the differences in solubilities are only small and to a first approximation the dissolution of Sr-Ca metastable phases may be regarded as a congruent one.

Solubility products (in distilled water) for the mineral phases of interest are as follows (Krauskopf, 1967): $MgCO_3$ $10^{-5.1}$, $MgCO_3 \times 3H_2O$ $10^{-5.6}$, $CaCO_3$ (aragonite) $10^{-8.22}$, $CaCO_3$ (calcite) $10^{-8.35}$, $SrCO_3$ $10^{-9.6}$. This would support the conclusion about distinct incongruent dissolution of $MgCO_3$ vs. $CaCO_3$ and $SrCO_3$ and would also indicate only a slight difference in solubilities of the Ca-Sr phases. The dissolution of the $CaCO_3$-$SrCO_3$ pair is also complicated by the presence of $SrSO_4$ ($10^{-6.5}$) and $CaSO_4$ ($10^{-4.5}$) or $CaSO_4 \times 2H_2O$ ($10^{-4.6}$) in the rocks. This and some other factors, might account for the erratic behaviour in solubility of Sr and Ca in carbonate rocks. To explain the decreasing Sr/Ca ratio with increase in diagenetic alteration, the suggestion of Kinsman (1969) might be accepted. Since the saturation of waters with respect to calcite or aragonite is reached relatively easily, further dissolution is limited only to Sr (and other unsaturated elements, such as Mg). In repeated dissolution, this would lead to a decrease in the Sr/Ca ratio of the rocks. An alternative process might be multiple dissolution and precipitation of carbonate rocks. Due to the partition coefficient of Sr between solution and solid (<1), this might lead to a gradual decrease of Sr content in the rocks.

Accepting the solution-precipitation hypothesis and a congruent dissolution as a first order approximation of the Sr/Ca relation (in view of the uncertainties in other parameters the small differences in solubility would not be important anyhow) it is possible to predict Sr behaviour in certain limited conditions.

It is apparent that in the above model the Sr content of the stable carbonate phase will depend primarily on the Sr content and mineralogical mode of the original carbonate phase and on the composition and volume of the intervening solutions (pore waters). The origin of pore waters is limited principally to pore waters of marine and meteoric origin.

Flügel and Wedepohl (1967), Wedepohl (1969b) and mainly Kinsman (1969) developed models of Sr behaviour for the so called open and closed systems of diagenesis. In their opinion the open systems of diagenesis are by far the most common among sedimentary carbonate rocks, and so the models have very restricted predictive value. This statement was disputed by Veizer and Demovic (1969, 1970 and in press) and Veizer et al. (1971). They argue that the "closed" system of diagenesis (as defined in their "in press" paper and also in the discussion in Appendix 3) is quite important, and where this is so, the predictive value of Sr concentrations for interpretation of original mineralogy might be improved quite considerably.

There are four lines of evidence suggesting "closed" system of diagenesis.

(a) Textural and structural data.

The preservation of textural and structural features in the accepted "wet" conditions is in favour of a "closed" system of diagenesis.

(b) Oxygen and carbon isotopes.

According to Degens (1967) the C isotope distribution once fixed in the carbonates is apparently not significantly altered during diagenesis and metamorphism. There can be changes of $\delta^{18}O$ with diagenesis, but in some environments the original values are apparently preserved, even in Paleozoic rocks.

Fabricius et al. (1970) and Kaltenegger (1967) showed that original Mesozoic aragonitic material which has been calcitized in nearly every case did not change $^{18}O/^{16}O$ ratios during this process.

The above discussion indicates that the carbonate system in many cases may be regarded as a "closed" one.

(c) Sr isotopic data.

It was shown by Veizer (1970a), that the Triassic carbonate rocks of the Western Carpathians indicate different Sr^{87}/Sr^{86} ratios for different rock types and sedimentary environments. The differences are not limited only to the different rocks and/or environments, but there are also consistent variations with time for the same type of rock (fig. 36). In particular the southern part of the Anisian-Norian carbonate platform (Veizer, 1970a, fig. 4 and 10) formed quite permeable interconnected hydrodynamic unit. The consistent variations in Sr^{87}/Sr^{86} ratios for different stratigraphic horizons of the same type of rocks hardly could be preserved in an open system type of diagenesis.

Peterman et al. (1970) determined Sr^{87}/Sr^{86} of fossils from shales and limestones. The ratios for contemporaneous samples were similar, although the Sr isotopic ratios of the host rocks were vastly different. This again supports the "closed" system of diagenesis.

(d) Sr abundance data.

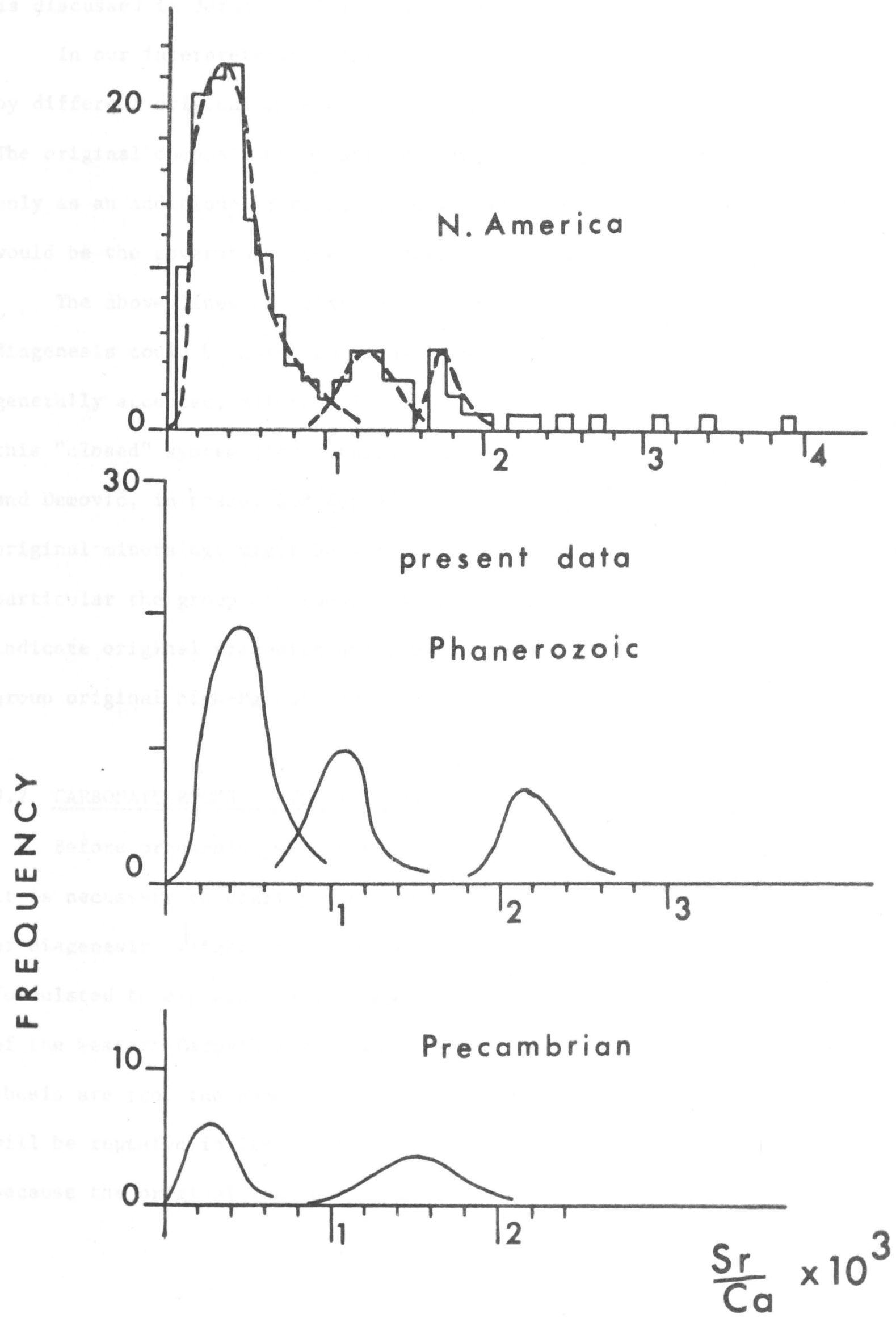
Sr has been observed to be highly fractionated among organic textures, matrix and cement within the same sample (Flügel and Wedepohl, 1967; Kulp et al., 1952; Veevers, 1969b). This would hardly be so in an open system of diagenesis.

Veizer et al. (1971) discussed pelagic Malmian-Neocomian samples of the High Tatra Mantle Series. They concluded that their alteration by continental waters is unlikely, yet their Sr content is very low (~150 ppm). With sea water derived pore solutions and an open system of diagenesis the final stable phase should have ~1000 ppm of Sr. The alternative is to assume a "closed" system of diagenesis (see Appendix 3) and presence of high-Mg calcite as a cement. Its solution and precipitation of low-Mg calcite might lead to Sr values encountered in the rocks (Veizer and Demovič, in press). Similarly Goldberg and Bonatti (1970) observed conversion of original high-Mg

calcite into low-Mg calcite after its transport into deep sea, as indicated by oxygen isotope data. The Sr content of the low-Mg calcite was 350-590 ppm. This low value again could not be achieved in an open system in equilibrium with sea water.

The average molar ratio $(^{m}Sr/^{m}Ca)_{L}$ of surface continental waters is 0.32×10^{-2} (Kinsman, 1969). This ratio would be modified in ground waters, generally leading to higher values. Nevertheless, the limestones would be in equilibrium with the average Sr value in continental waters, and one would expect the majority of Sr values in limestones to cluster around 400 ppm if the open system of diagenesis is predominant. The average Sr content of carbonate rocks is indeed close to this value (Table 2). On closer examination of data, however it seems, that this is only a pooled average of two or more distinct groups of limestones and/or dolomites with average Sr content $\sim$600 and $\sim$200 ppm. The rocks with Sr values around 400 ppm are in fact quite deficient. Such a bimodal grouping is clear in data of Veizer et al. (1971), Veizer and Demovic (in press) and in figure 52 in Appendix 3. There are indications of this grouping also in the data of Kulp et al. (1952) for N. American limestones. In their histogram of $(Sr/Ca) \times 10^{3}$ ratios (fig. 34) one may observe a marked minimum in values close to 1 ($=\sim$400 ppm). The bimodal or polymodal distribution is not so apparent in the present samples (fig. 3) because of their very wide spread in ages and thus different influences of diagenetic factors, which will be discussed later. However, the bimodal or polymodal distribution becomes immediately evident when the limestones are divided into Phanerozoic and Precambrian groups (fig. 34). The presence of the dominant group of limestones with $\sim$200 ppm of Sr ($(Sr/Ca) \times 10^{3} \sim 0.5$) would demand either very high quantities of "distilled" (i.e., rain) water as a major diagenetic fluid, since the Sr value is too low by a factor of 2 to be in equilibrium with the average continental water,

Figure 34. Histograms of (Sr/Ca) x 10^3 distributions in limestones. The graph for North American limestones is a modified diagram of Kulp et al. (1952).



or a "closed" system of diagenesis with presence of high-Mg calcite. The first assumption is probably not very realistic. The second assumption is discussed in detail by Veizer and Demović (in press and Appendix 3).

In our interpretation, the bimodal grouping of Sr values was caused by different original mineralogy and the "closed" system of diagenesis. The original composition of pore waters, although important, was regarded only as an additional factor, since the dissolution of unstable phases would be the governing cause of their chemistry.

The above lines of evidence indicate that the "closed" system of diagenesis could be more common among sedimentary carbonate rocks than generally accepted, although it is not necessarily dominant. Accepting this "closed" system (for detailed calculations see Kinsman, 1969, Veizer and Demović, in press, and Appendix 3) attempts to interpret the overall original mineralogy might be more realistic than previously believed. In particular the group of limestones with high Sr concentrations might indicate original aragonite and low-Mg calcite composition and the low Sr group original high-Mg calcite mineralogy.

9.2 CARBONATE ROCKS OF THE WESTERN CARPATHIANS AND THEIR DIAGENETIC MODEL

Before proceeding with the systematic discussion of the present samples it is necessary to clarify the meaning of the "closed" and "open" systems of diagenesis (Veizer and Demović, in press). The models were originally formulated to explain the bimodal distribution of Sr in the Mesozoic rocks of the Western Carpathians. Since the Mesozoic samples in the present thesis are from the same rock types, it is inevitable that the discussion will be repeated in its basic points. This is done in Appendix 3, mainly because the original manuscript of Veizer and Demović was mailed by the

editor to Bratislava and was lost during this process. The section "Systematic description of rocks" is a continuation of the discussion in Appendix 3.

Veizer and Demovič (in press and Appendix 3) warned against the use of single samples for interpretation, and yet several samples in the present thesis are discussed in this manner. In the case of the Mesozoic samples the values presented here are representative of the average Sr concentrations for the particular rocks (Demovič and Veizer; 1000 unpublished analyses). In the case of Silurian samples this is done only because of the lack of mean values due to the variability of rock types.

In all subsequent discussion the calculations will be based on the distribution coefficients listed below. The distribution coefficients "k" in the formula $(^{m}Sr/^{m}Ca)_S = k \times (^{m}Sr/^{m}Ca)_L$ are the following:

aragonite at 25°C 1.13 (Kinsman and Holland, 1969; Kinsman, 1969)

calcite at 25°C 0.14 (Kinsman, 1969)

The distribution coefficient between dolomite and aragonite at 120°C is 97 (Usdowski, 1970). To my knowledge, no distribution coefficients are available for coexisting dolomite and solution or calcite and dolomite. Winland (1969) reports a distribution coefficient of 0.02 for $MgCO_3$ between sea water and high-Mg calcite.

9.3 SYSTEMATIC DESCRIPTION OF ROCKS

The high Sr content of the Quaternary and Tertiary samples (Appendix 1) is presumably due to the presence of aragonite. Assuming that all Sr and Ca are associated with the carbonate fraction (true only to a first approximation), the caliche sample was precipitated from solution with $(^{m}Sr/^{m}Ca)_L = 0.37 \times 10^{-2}$. The sample was collected on argillaceous rocks and both Sr and Ca were leached from shales, very likely by rain water, and

reprecipitated at the surface by evaporation. The high Sr^{87}/Sr^{86} ratio (0.7168) is consistent with origin of Sr from shales. Average shale of Turekian and Wedepohl (1961) has $(^{m}Sr/^{m}Ca)_{S} = 0.62 \times 10^{-2}$. This might indicate a preferential solution of Ca from the shale, which is in agreement with the known solubility products for the carbonates and sulphates of these two elements (Krauskopf, 1967).

The majority of the West Carpathian Mesozoic rocks or their equivalents were discussed in detail in papers of Veizer and Demovič (1969 and in press), Veizer et al. (1971) and in Appendix 3, and there is no need of further elaboration. The prediction of higher Sr content for early diagenetic dolomites, compared to the late diagenetic ones is well illustrated (515, 141, 109, 119 vs. 46, 113 and 53 ppm). Due to the high sensitivity of the partition coefficient to temperature (Usdowski, 1970) it is difficult to estimate Sr content of the original aragonite. However, the value ~9800 ppm for "hypersaline" aragonitic muds (Kinsman, 1969) seems to be consistent with the observed Sr concentrations in early diagenetic dolomites.

The Mesozoic samples not included in the previous discussion are treated below. The Doggerian-Malmian silicitic limestone (No. 13) is pelagic sediment overlain by a thick sequence of Malmian-Neocomian pelagic limestones. Fresh water syn- or anadiagenetic alteration of this rock is very unlikely. Its $(Sr/Ca) \times 10^{3}$ ratio (0.729) is too low to be consistent with original aragonitic or low-Mg calcitic nature in a "closed" system of diagenesis. Liquid from which the sample might have been precipitated should have $(^{m}Sr/^{m}Ca)_{L} = 0.24 \times 10^{-2}$, which is too low to be in equilibrium with either sea water or majority of continental water derived pore solutions. The presence of high-Mg calcite in original sediment might help to establish the required $(^{m}Sr/^{m}Ca)_{L}$ value, however the association of limestones with radiolarites points to their abyssal depositional environment. High-Mg

calcite has not yet been reported in substantial quantities from similar recent sediments. Their epidiagenetic alteration by meteoric waters is also very unlikely, since the rocks are very dense and impermeable. So the very low Sr content remains an enigma for future studies. There is a chance that the rocks were deposited in a substantially shallower environment, since the radiolarites might have been related to the traces of contemporaneous submarine volcanism (Andrusov, 1964; Mahel' and Buday, 1968). This would permit the presence of the high-Mg calcite required.

The high Sr content of the Rhaetian sample (No. 17) and low Sr values for the Triassic samples of the Gemeridy Unit (18, 24, 25 and 28) could be explained by similar factors to those discussed in the case of their type equivalents (Veizer et al., 1971 and Veizer and Demovic', in press and Appendix 3).

The Permian and Carboniferous brachiopods were formed originally by (low-Mg?) calcite (Lowenstam, 1963). This original calcitic mineralogy was confirmed by discovery of Carboniferous organic skeletons in which the primary mineral phases were preserved (Stehli, 1956). Their high Sr content would be consistent with their supposed low-Mg calcitic composition and the "closed" system of diagenesis.

The low Sr content of Carboniferous and Devonian reef-like sequences could be explained in similar manner to the low values in equivalent Triassic rocks (Veizer and Demovic', in press and Appendix 3).

The Devonian stromatolitic limestones (Cavan Bluff Limestones) contain extremely high Sr concentrations. The highest $Sr/Ca \times 10^3$ ratio (7.07) would require $(^mSr/^mCa)_L = 2.29 \times 10^{-2}$. This value is too high for majority of surface and ground waters as well as for sea water. This would practically exclude the "open" system of diagenesis from consideration. Presence of any type of calcite as the original phase may be excluded, since its solution

or preservation could not lead to such high Sr concentrations. Solution of an original aragonite (~9800 ppm) in a "closed" system of diagenesis, precipitation of stable calcite (~1400 ppm) and the resulting "build up" of Sr/Ca in the residual solution might lead to the $(^{m}Sr/^{m}Ca)_{L}$ required.

The assumption about original aragonitic mineralogy of stromatolites is consistent with the overall slightly "hypersaline" nature of the sequence (Murrumbidgee Series). The blue-green algae could cause precipitation of aragonite by their organic processes. Logan (1961) suggested that at least the domed and club-shaped stromatolites form as a result of the precipitation of acicular aragonite cement.

It might be argued that the high Sr content might be caused by the presence of celestite. Even if this assumption is confirmed, it would not necessarily eliminate the above interpretation. Saturation with respect to celestite is not reached even during gypsum precipitation (Braitsch, 1971 p. 208), and thus celestite cannot be regarded as a primary phase of carbonate rocks. So if present, it could have formed as a diagenetic product during alteration of aragonite to calcite.

The Hume Series limestones (Silurian) show also bimodal Sr distribution: high contents in samples 63, 64, 65, low contents in 67, 68, 69 and intermediate content in 66. The low Sr contents appear compatible with the general hypothesis, since the crinoid ossicles were very likely formed of high-Mg calcites, as are their recent relatives (Graf, 1960; Lowenstam, 1963). The high Sr content of the dark unfossiliferous micrite (No. 63) also appears compatible (cf. Veizer, 1970a and Chapter 2). This rock is believed to be of bacterial origin and as such is likely to have been precipitated as aragonite (Greenfield, 1963).

Although present Anthozoa are aragonitic, the shell mineralogy of Paleozoic ones was probably calcite (Lowenstam, 1963; Stehli, 1956; Boggild,

1930). On the basis of Sr content (No. 64) one cannot discriminate between the two alternatives. The Sr content of sample No. 65 is surprisingly high. On the basis of its petrology (crinoidal biosparite) one would expect values comparable to the other crinoidal limestones (~200 ppm). Since both samples of Hume Limestones (64 and 65) were very porous and permeable and their Sr/Ca ratios are close to the equilibrium value with sea water, an "open" system of diagenesis in the presence of sea water or sea water derived pore solutions might be the best explanation of their high Sr values.

The generally high Sr/Ca ratios of the Gordon Limestones (Ordovician) are in agreement with their interpretation as a predominant bacterial and/or partly algal aragonitic precipitate. The decrease in $(Sr/Ca) \times 10^3$ ratios to values of ~1 might be explained by their considerable age and so by a certain degree of epidiagenetic alteration under the influence of ground waters.

The Cambrian rocks show almost exclusively low Sr values. This may be attributed partly to their age, as was already pointed out in the case of Ordovician, and probably partly to their predominant original high-Mg calcitic composition. To my knowledge, there are no data on possible original mineralogy of the Cambrian Archaeocyatha, which are very common in the majority of the rocks. A high state of textural preservation is regarded as an indication of original calcitic mineralogy (Boggild, 1930). Their extremely well preserved texture in some of the thin-sections might support the calcitic interpretation. It is also quite probable, that their permeable reef-like texture was cemented by high-Mg calcite, as is the case with recent algal reefs (cf. DeGroot, 1969; Taylor and Illing, 1969; Veizer and Demović, in press).

The very high Sr value of the sample No. 100 (1215 ppm) might be possibly related to its probable stromatolitic origin. Since only one sample was collected, no firmer conclusion can be reached in this case.

The above description and interpretation could well be optimistic. The majority of the samples are consistent with the theory outlined in Appendix 3. However, consistency is not still proof of the theory, and its acceptance or rejection requires further testing. Especially in the case of permeable structures, such as reefs, the alteration by meteoric waters is quite possible, and the degree of "open" system of diagenesis is very difficult to determine. Therefore the interpretation is extended only as a working hypothesis in the knowledge that the explanations given here might not be unique.

The Precambrian rocks are almost completely formed by stromatolitic limestones and early diagenetic dolomites (see Chapters 2 and 3). Therefore one might expect high Sr values in limestones and values about 100 ppm or more in dolomites. The Sr content is of course dependent on the age of the rocks and so on the degree of their epidiagenetic alteration.

For the rocks of the Adelaidean Geosyncline the above assumption is valid almost without exception. Sample No. 126 (2015 ppm) is a vein of secondary calcite in the rock No. 125 (697 ppm). Since the vein was derived from the surrounding rocks (calcareous siltstone No. 125), its formation may be used for calculation of the leaching efficiency for Sr and Ca. The $(^{m}Sr/^{m}Ca)_{L}$ required for the precipitation of the calcite vein is $\geqslant 2.07 \times 10^{-2}$. The value obtained by dissolution of the surrounding rock is 0.24×10^{-2}. This would indicate an incongruent dissolution of the source rock with substantially higher solubility of Sr than Ca. Thus, with respect to Sr and Ca the dissolution of carbonate is very likely different from that of shales, as indicated by the formation of caliche. The different behaviour

of Sr is possibly related to its association with silicates in shales and with carbonates in calcareous siltstones, whereas Ca in both cases is present mainly as a carbonate.

All Australian rocks older than about 1 b.y. have low Sr concentrations. This feature might be expected in view of their great age and predominantly dolomitic composition. Nevertheless, the low Sr content of the Bitter Springs Formation is surprising. The rocks are petrologically very similar to the rocks of the Adelaidean Geosyncline. The difference in age of the two sequences is uncertain, but might be ~200 m.y. or possibly less. The expected higher degree of epidiagenetic alteration related to the age difference does not seem to justify the difference of an order of magnitude in their Sr content. Even more surprising is the similar Sr content of limestones and dolomites for the majority of samples. Sample No. 161 contains a very high proportion of secondary calcite veins and this may be a reason for its high Sr concentration. The remaining samples would require $(^{m}Sr/^{m}Ca)_{L}$ as low as 0.0037×10^{-2}, which is clearly too low for majority of natural and pore waters, unless there was a drastic change of Sr/Ca ratio of sea water at about 900 m.y. The last possibility does not seem to be very realistic. The required $(^{m}Sr/^{m}Ca)_{L}$ values could be obtained by dissolution of limestones with Sr content ~300 ppm in very diluted solutions. Even so an "open" system of diagenesis would have to be maintained to prevent the build up of the Sr/Ca ratio of the residual solution.

In thin-sections several samples showed features of recrystallization. The northern boundary of the Amadeus Basin, from which the samples were collected, was also affected quite strongly by tectonic processes (Forman, 1971). This might point to a tectonically induced recrystallization as a major factor in the low Sr content of the limestones. This process might lead to an "expulsion" of impurities (Sr) from the rocks (as in the formation

of marbles). This interpretation might also be supported by the extremely high oxidation state (Fe^{3+}/Fe^{2+}), and several other inconsistent geochemical data for the Bitter Springs Formation. On the other hand, to maintain a balanced view, one has to acknowledge the absence of marked macroscopic textural features, and this might argue against the tectonic interpretation.

Therefore, the Sr content of the Bitter Springs Formation might indicate a tectonically induced recrystallization, but this cannot be yet proved.

Strontium concentrations of the Steep Rock Lake and Bulawayan Limestones are remarkably high in view of their great age and the mild metamorphism of the Bulawayan System (Chapter 2). It is difficult to conclude why this is so, because there are vast uncertainties in interpreting the original mineralogies of these rocks and the compositions of the atmosphere and hydrosphere in earlier Precambrian times. Their unique Sr^{87}/Sr^{86} ratios appear to argue against their "open" system alteration at a later stage of their epidiagenetic history. The $({}^{m}Sr/{}^{m}Ca)_{L}$ required for the Bulawayan Limestone would be about 0.95×10^{-2} if the original phase was stable low-Mg calcite and could be substantially less in the case of aragonite. Although the above value is close to the present sea water ratio (0.86×10^{-2}) no conclusion can be based on these data.

The extensive discussion of Sr distribution has indicated, in many cases, its consistency with the "closed" system model of diagenesis. If true, this would strongly support interpretation of Sr^{87}/Sr^{86} ratios as being inherited in their major part from the Sr isotopic composition of the parent solution. This might form a strong basis for studies of Sr isotopic evolution of the parent solutions (sea water?) during the Earth's history. The topic will be discussed in Chapter 10.

9.4 VARIATIONS WITH TIME

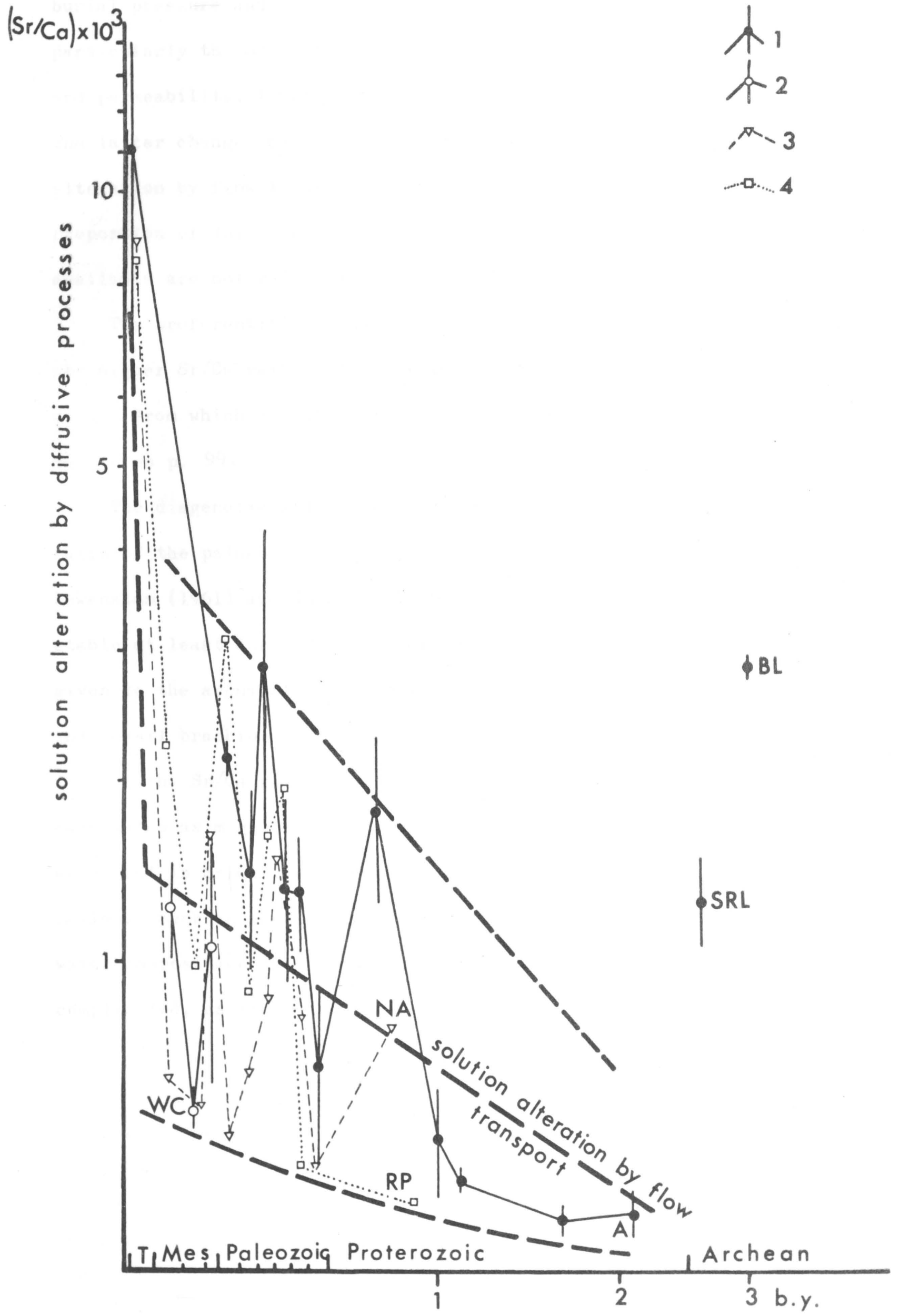
The decrease in Sr content with increasing age of the rocks is obvious from fig. 35. This trend is typical for all the data available with the exception of the Archaean data. The extremely high Sr contents of these samples are surprising and no satisfactory explanation is as yet available. To postulate a very small degree of diagenetic alteration does not seem to be a full answer, since the Bulawayan System for example is slightly metamorphosed.

The decreasing Sr content can be explained by preferential loss of Sr with increasing degree of diagenesis (see p. 87 and also Turekian, 1964 and others). Wolf et al. (1967) proposed that the trend might be due to the chemical evolution of the sedimentary crust. Although the increasing proportion of dolomites in older sequences might account for somewhat lower Sr/Ca ratio, the latter alternative cannot explain the magnitude of this decrease. The trend is also quite obvious within limestone as well as dolomite groups and thus is independent of lithology.

The decrease in Sr content probably occurs in several discontinuous steps. After a sharp decrease in the Quaternary and Tertiary, the loss of Sr during older periods is much less pronounced (fig. 35). The initial sharp decrease is due to the disappearance of unstable carbonate minerals, predominantly aragonite. This sharply lowers the Sr/Ca ratio by one order of magnitude (solution alteration by diffusive processes - Sippel and Glover, 1964).

The scatter of data above and below the regression line could, in my view, be explained by differences in original mineralogy of the rocks. Accepting the "closed" system model of diagenesis, the original aragonites and stable low-Mg calcites would be concentrated above the regression line, whereas the predominantly high-Mg calcites might be concentrated below.

Figure 35. Variations of (Sr/Ca) x 10^3 ratios with geological age.
Explanations:
(1) Australian carbonate rocks (present thesis)
(2) carbonate rocks of the Western Carpathians (present thesis),
(SRL) Steep Rock Lake Limestones (present thesis),
(BL) Bulawayan Limestones (present thesis),
(3) carbonate rocks of the Russian Platform (Vinogradov et al., 1952),
(4) carbonate rocks of North America (Kulp et al., 1952).
The vertical bar represents 1σ limit of the mean.


(Sr/Ca)x10³
10
5
1
solution alteration by diffusive processes
1
2
3
4
BL
SRL
NA
WC
RP
A
solution alteration by flow transport
T
Mes
Paleozoic
Proterozoic
Archean
1
2
3 b.y.

Once the stable mineral assemblage is established (~50-100 m.y.), increasing burial pressure and temperature cause remobilization of a part of the Ca and particularly the Sr, but this process is much slower due to the lower porosity and permeability, lower water content and higher stability of minerals. The latter changes are achieved mainly through the so called solution alteration by flow transport (Sippel and Glover, 1964). With increasing proportion of dolomites, the slope may be somewhat different, but the data available are not yet sufficient to permit more extensive speculation.

The preferential leaching of Sr with respect to Ca was apparent from the higher Sr/Ca ratios of the veins compared to the surrounding carbonate rocks, from which the veins were derived. The problem was discussed in detail on p. 99.

The diagenetic alteration complicates an attempt to estimate the Sr/Ca ratio of the palaeo-seawater. In accordance with views of Odum (1957), Lowenstam (1961) and Turekian (1964), this ratio is regarded as relatively stable at least during the Phanerozoic history of the Earth. Priority is given to the argument of Lowenstam based on similar Sr/Ca ratios of Recent and fossil brachiopods.

If the Sr/Ca ratio of sea water is determined largely by the recycled carbonates as might be indicated by Sr isotopic data, there should be an agreement in Sr/Ca input (continental waters) and output (sedimentation) ratios. Such an equilibrium is demanded by the steady state model of sea water composition discussed in Chapter 8. The relations are however more complicated, as indicated by the following table:

Table 6

$(^{m}Sr/^{m}Ca) \times 10^{2}$ ratios of different types of rocks and waters	
average crust[1]	0.42
basalt[1]	0.32
granite[1]	0.81
shale[1]	0.44
limestone[2]	0.05 - 0.07
dolomite[2]	0.03
aragonite in equilibrium with sea water[3]	0.94
calcite in equilibrium with sea water[3]	0.12
sea water[3]	0.86
average continental water[3]	0.32

1 - calculated from the average concentrations of Krauskopf (1967)
2 - calculated from Table 2
3 - Kinsman (1969)

Several observations are immediately apparent from this table. Sr/Ca ratio of continental water is substantially higher than that of carbonates. A part of this controversy might be possibly explained by continuous leaching of Sr after the saturation with respect to Ca was achieved or by the partition coefficient (p. 89 and Kinsman, 1969). A major reason for the high Sr/Ca ratio might be the solution of other rocks as indicated by Sr^{87}/Sr^{86} of such waters (Table 8). If the conclusion about lower leaching efficiency of Sr, compared to Ca, from shales is applicable to majority of shales and not only to caliche formation, igneous rocks could be assumed to be the source of additional Sr. Their high Sr/Ca ratios would be consistent with this interpretation.

At present the bulk of carbonate deposition is in the deep sea and this is sufficient to accommodate almost all Ca supplied by streams (Turekian, 1964). The Sr/Ca ratio of deep sea limestones (≈0.12) is not sufficient to accommodate all the Sr. In order to maintain the steady state conditions of sea water, additional Sr sinks are required. Shallow water carbonates with high proportions of aragonite (but also high-Mg calcite) could be considered as such alternative sinks. However, the aragonites are unstable and their transition to calcite during an early stage of syndiagenesis would cause "expulsion" of Sr and its return into the sea by a short cut, without involvement of surface continental waters. The period of this alteration is in general much shorter than the residence time of Sr in sea water (≈20 x 10^6 y - Goldberg, 1963). Such a shallow water carbonate sink would also demand large quantities of Ca, which is already bound up in the deep sea types. This might indicate the importance of clays as potential Sr absorbers. Their sheer volume might support such an interpretation. Another indication of the importance of clays in Sr cycle might be obtained from consideration of the pre-Malmian history. There are no deep sea carbonates known from sequences older than Late Jurassic, yet the steady state conditions of sea water with respect to Sr/Ca ratio has been maintained at least since Mississippian (Lowenstam, 1961). The weathering cycle might have been different from the present one. Thus the much higher proportion of shallow water carbonates in pre-Malmian sedimentary sequences (compared to the present state) might have been in some sort of equilibrium with such a changed weathering cycle. Accepting the role of aluminosilicates in Sr and Ca cycles, the secondary postulates would not be necessary.

Due to the possible changes in the solubilities of Ca and Sr and a much smaller proportion of carbonates in Precambrian sequences, the overall

Sr/Ca budget might have been different from the present situation and thus it is difficult to estimate the Sr/Ca ratio of Precambrian oceans.

Chapter 10

STRONTIUM ISOTOPES

10.1 DISTRIBUTION OF Sr ISOTOPES IN CARBONATE ROCKS

The positive correlation coefficient of Sr^{87}/Sr^{86} ratios with MgO (Table 3) indicates higher ratios in dolomites. This is also apparent from the histograms in fig. 4. Whereas the values for limestones are distributed normally with the mode at 0.7085, the ratios for dolomites form either several normal or one negatively skewed lognormal population with the mode at 0.7105. Since the dolomites contain a higher content of insoluble residue than the limestones, the higher isotopic ratio might be due partly to acid leaching of radiogenic Sr from the aluminosilicate phase during carbonate extraction. However this can be only a partial explanation of their higher ratios. As will be discussed later, the different values might reflect also original differences in Sr^{87}/Sr^{86} of their respective sedimentary environments, and/or diagenetic equilibration and alteration. Since the environments required for the formation of early diagenetic dolomites usually have only a limited exchange of water with the open sea (Friedman and Sanders, 1967) and since such environments are very susceptible to an influx of land derived substances having more radiogenic Sr, their higher ratios might be expected. The late diagenetic dolomites are within the limits of limestone ratios.

10.2 DISTRIBUTION OF Sr ISOTOPES IN WATERS

The overwhelming majority of sedimentary carbonate rocks are sea water precipitates. It is thus necessary to discuss the distribution and behaviour of Sr isotopes in sea water and their subsequent diagenetic alterations. The Sr isotopic composition of sea water is summarised in Table 7. The

Table 7. Sr^{87}/Sr^{86} of sea water

Author	Sr^{87}/Sr^{86} of sea water and marine shells		Sr^{87}/Sr^{86} of the Eimer and Amend Standard	
		σ		σ
Peterman et al. (1970)	(19) $0.7089_8 \pm 0.0003_7$ $^{x}0.7092_1$		Pacific, Atlantic, Indian and Arctic Oceans	(5) $0.7079_1 \pm 0.0001_2$
Hamilton (1966)	(9) $0.7088_9 \pm 0.0004_9$ $^{x}0.7090_8$		Atlantic Ocean	(6) $0.7079_5 \pm 0.0002_4$
Faure et al. (1965)	(12) $0.7093_0 \pm 0.0005_0$ $^{x}0.7090_4$		N. Atlantic Ocean	(9) $0.7084_0 \pm 0.0003_0$
Murthy and Beiser (1968)	(23) $0.7094_0 \pm 0.0006_3$ $^{x}0.7092_5$		Pacific, Atlantic, Indian Oceans	(8) $0.7082_9 \pm 0.0003_9$
Kaushall and Wetherill (1969)	(9) $0.7094_8 \pm 0.0004_1$ $^{x}0.7093_5$		do	(6) $0.7082_7 \pm 0.0004_1$
Hildreth and Henderson (1971)	(1c) 0.7090_5 $^{x}0.7092_1$			(1c) 0.7079_8
Faure et al. (1967)	(8) $0.7093_0 \pm 0.0003_0$ $^{x}0.7093_4$		Hudson Bay	(5) $0.7081_0 \pm 0.0003_0$
This thesis	(2) $0.7093_5 \pm 0.0000_9$		Coorong Lagoon	(9) $0.7081_4 \pm 0.0000_4$
	(8c) 0.7092_3	$\sigma_{mean} = 0.0002_3$		0.7081_4

Explanations:

(9) - No. of analysed samples, (8c) - No. of analysed composite samples

$^{x}.7093_4$ - value normalised to E + A $=0.7081_4$

table documents the conclusion of previous authors that sea water is very well mixed with respect to Sr isotopes. This property is well established not only for the open sea with vigorous circulation, but supported also by the indistinguishable Sr^{87}/Sr^{86} values for such semi-barred basins as Hudson Bay (Faure et al., 1967) and Coorong Lagoon (this thesis). According to Faure et al. (1967) carbonate shells have similar Sr^{87}/Sr^{86} ratios as the aqueous environments in which the shells are secreted. Analyses of fresh water Sr isotopic composition (Table 8) indicate average Sr^{87}/Sr^{86} of 0.7154 ± 0.0035. However the range of the ratios is very high, depending on the petrological composition of the catchment area. The average value quoted for fresh waters may be too high, since the drainage area is mainly the old Canadian Shield with high radiogenic Sr content. In theory one might expect Sr^{87}/Sr^{86} variations of continental waters to be anywhere between 0.704 (mantle? derived basalts) and 0.740 (old granitic plutons). In practice, due to the much higher solubility of carbonate rocks and disseminated carbonate in other sedimentary rocks, the values would probably cluster between that of sea water (0.709) and 0.720. Nevertheless one may conclude that a substantial dilution of sea water by continental water should lead to higher Sr^{87}/Sr^{86} ratios. However, the difference in Sr content of sea water and fresh waters is very high (8 ppm vs. ~ 8-100 ppb) (Faure et al., 1967; Compston and Pidgeon, 1962) and so the contribution of Sr from fresh water is in general negligible. Even a dilution of 50% would alter the Sr^{87}/Sr^{86} of sea water by only about 1% of the difference between the two ratios.

From the above discussion, it seems probable that the Sr isotopic ratio of sea water cannot be altered easily even in semirestricted marginal basins. During arid periods, which are typical for carbonate sequences with high dolomite content, the susceptibility to alteration may be even lower

Table 8. Sr^{87}/Sr^{86} of fresh waters

	Sr^{87}/Sr^{86} of fresh waters and fresh water shells	Sr^{87}/Sr^{86} of the Eimer and Amend standard
Faure et al. (1963) N. Ontario		σ
Kenoran Orogeny	(5) 0.721 ± 0.005 $x_{0.7183}$	(16) 0.7108 ± 0.0002
Hudsonian Orogeny	(2) 0.720 ± 0.002 $x_{0.7173}$	do
Grenville Orogeny	(6) 0.718 ± 0.004 $x_{0.7153}$	do
Great Lakes	(4) 0.7139_1 ± 0.0034 $x_{0.7112}$	do
St. Lawrence River	(2) 0.714 ± 0.005 $x_{0.7113}$	do
Appalachian Province	(1) 0.7137 $x_{0.7110}$	do
Hart and Tilton (1966)		
Lake Superior	(3) 0.7165 ± 0.0021 $x_{0.7164}$	(1) 0.7082 ± 0.0007
Faure et al. (1967)		
Payne River	(1) 0.721 $x_{0.721}$	(5) 0.7081 ± 0.0003
This thesis		
Amadeus Basin (caliche)	(1) 0.7168_4 ± 0.0002_0	(9) 0.7081_4 ± 0.0000_4
	(9c) 0.7154_4 σ_{mean} 0.0035_4	0.7081_4

Explanations as in Table 7

due to the low discharge of continental waters. However the arguments are not conclusive, since there are no equivalents at the present time of the large epicontinental seas which are believed to be more typical of the geological past (i.e. the Zechstein of Europe).

10.3 DIAGENETIC INFLUENCES

During the discussion of the diagenetic behaviour of elementary Sr, it was argued that carbonate rocks were subjected to a "closed" system of diagenesis in many cases. The Sr isotopic evidence in its favour has been already quoted (p. 90). A "closed" system of diagenesis would retain the average of the original Sr isotopic ratios.

Disregarding, nevertheless, the "closed" system and accepting the open one as the prevailing diagenetic type, it may still be possible to obtain reliable data for Sr^{87}/Sr^{86} in the original solution. In an open system under the influence of sea water and solutions derived from sea water, the diagenetic alteration of rocks might lead to mineralogical and chemical changes, but a substantial change in Sr^{87}/Sr^{86} is unlikely, since the stable phases would acquire the ratio of the intervening sea water. The time difference between sedimentation and syndiagenesis is comparatively short and so it is unlikely that substantial variations in average sea water ratios would develop. It might be argued that the trapped solutions would be modified by surrounding rocks. Carbonate rocks are generally associated with other sea water precipitates and clastic sedimentary rocks, mainly shales. It was shown by Dasch (1969) and Biscaye and Dasch (1971) that there is little Sr isotopic equilibration between clay minerals and sea water in recent marine clays and consequently the influence of surrounding rocks should not be high. Disregarding the last argument, the interaction with surrounding rocks could lead either to similar Sr isotopic ratios

(i.e. sea water precipitates) or to higher values (i.e. shales). Possibly the only case in which the intervening waters might acquire ratios lower than sea water would be in the presence of high proportion of volcanics or hydrothermal solutions with low Sr^{87}/Sr^{86} ratios. The last two possibilities can be relatively easily evaluated in particular cases and accepted or rejected. Concluding this discussion, one may postulate that in an open system of diagenesis under the influence of sea water or sea water derived solutions, the observed Sr^{87}/Sr^{86} ratios would be similar to their original values or higher. Since in any such reservoir with an easy exchange of elements the clay layers would be inevitably the major controlling factor of the intervening water composition, the case of higher ratios is a more probable one.

The previous discussion was confined to diagenesis sensu stricto (syn and early anadiagenesis). During later periods of deep burial anadiagenesis and epigenesis, the rocks may be subjected to a certain degree of exchange between silicate and carbonate phases initiated by load pressure. Such an exchange would be more important in fine grained rocks with higher content of clay minerals, and the probability of this exchange might also increase proportionally with increasing age. The rate of this process would very likely vary from specimen to specimen. This partial equilibration of phases does not necessarily involve surrounding rocks; instead, it might be confined to the carbonate and silicate phases of the same rock and so be of a closed system type.

If the carbonate and silicate phases were completely equilibrated during some stage of their depositional and diagenetic history, the silicate phase (clay), total rock, leach and carbonate would define an isochron with either the age of deposition or equilibration (cf. Bofinger et al., 1968). However this is not usually the case. Carbonate rocks are composed

of two distinctive phases with different Rb/Sr and $(Sr^{87}/Sr^{86})_0$ ratios. The $(Sr^{87}/Sr^{86})_0$ of the silicate phase is often between 0.710 and 0.720, since the silicates are in general formed by N + 1 stage clay minerals (Keller, 1970). Their Rb/Sr ratio is either reset during sedimentation and diagenesis, or inherited from older cycles. The carbonate fraction theoretically should have very low Rb/Sr ratios and the growth of radiogenic Sr should be minimal. Its Sr^{87}/Sr^{86} should not depart significantly from that of its original solution. During later stages of anadiagenesis and epigenesis, the load pressure might induce partial equilibration between both phases. The exact process is unknown, but might be possibly related to the higher solubility and mobility of carbonates and to the formation of such textural features as stylolites, cone-in-cone etc. The process will be very likely of a long-term duration and would proceed in multiple small steps. In rocks over 1000 m.y. old this is accompanied in all cases by preferential loss of Sr from the carbonate phase. This is in fact an open system of diagenesis with respect to Sr, although Rb is held in the system more strongly. Even the "closed" system of diagenesis as defined by Veizer and Demovic (in press) envisages some degree of Sr loss, however it is not by almost two orders of magnitude as is the case of the old rocks. This severely complicates, and possibly completely excludes, application of some types of correction to the actual measured Sr^{87}/Sr^{86} values of the leach. The problem will be discussed more specifically during systematic description later of particular suites of rocks.

10.4 LABORATORY LEACHING

In the laboratory treatment of samples, the dissolution of the carbonate might also dissolve part of the aluminosilicate phase with higher radiogenic Sr content. This problem might be more serious in the less

soluble dolomites having high insoluble residue content. The actual data do not support this possibility, since for almost any suite of samples the correlation between measured Sr^{87}/Sr^{86} of the leach and Rb/Sr of the total rock is either very weak or non-existent. Also the acid used was only 0.1 N HCl. Bofinger et al. (1968) demonstrated that there was no preferential leaching of radiogenic Sr^{87} during acid treatment of shales. Thus it is likely that this phenomenon will be of even less importance in carbonate rocks. However, if there is any preferential leaching of silicates, this also would lead to higher Sr isotopic values.

From the above discussion it seems reasonable to conclude that any possible alteration (during sedimentation, diagenesis and laboratory treatment) either would not effect the actual Sr^{87}/Sr^{86} ratios or would lead to an increase in measured values. A greater age since deposition has the same effect and correcting for age may be a serious problem for the older samples.

Building on the above conclusions one may postulate that for any suite of contemporaneous rocks, the lowest measured Sr^{87}/Sr^{86} ratio is the best approximation to the Sr isotopic composition of the well-mixed, contemporaneous sea water.

10.5 SYSTEMATIC DESCRIPTION

Quaternary

Sr isotopic composition of recent sea water and caliche was already discussed. The data were consistent with the previously published results (Tables 7 and 8).

Tertiary

One Miocene sample was analysed. The Sr^{87}/Sr^{86} of the Futuna Limestone (0.70926 with 2σ of 0.00016) is statistically identical with the Late

Miocene value of pelagic Foraminifera reported by Dasch and Biscaye (1971). Since both samples were analysed on the same machine, no correction is required. Due to the low Rb/Sr ratio and low age the age correction is negligible.

Following the discussion at the beginning of this chapter, as yet the best approximation to sea water Sr^{87}/Sr^{86} values are the data summarised in Table 9. The values of all authors are corrected to Eimer and Amend standard value 0.7081_4. 2σ for single measurements of Peterman et al. (1970) are taken as 0.0005_0.

Cretaceous

No post-Aptian samples were measured in the present set of data. The values of Late and Middle Cretaceous samples were again selected from literature (Table 9). Measured Early Cretaceous samples are summarised in fig. 36 and 37. The maximum age corrections are less than the 2σ limits of single measurements and are thus negligible. The Valanginian-Hauterivian ratio of Peterman et al. (1970) is preferred to my data because of the better 2σ limits.

Jurassic

Jurassic Sr^{87}/Sr^{86} ratios are presented in Table 9 and fig. 36 and 37. The maximum age corrections are again less than 2σ values.

The discrepancy between the Late Jurassic ratio of Peterman et al. and the data of this thesis is greater than 0.001. This is somewhat surprising, since the Western Carpathian Malmian samples are pelagic limestones. The material collected by Peterman et al. is the more suitable for isotopic studies, and the difference might be due to diagenetic factors already discussed. An alternative explanation could be a sudden variation in average sea water Sr isotopic ratio during the Jurassic, since the samples of Peterman et al. are of Oxfordian and the Carpathian samples of

Table 9. Preferred Sr^{87}/Sr^{86} ratios normalised to the Eimer and Amend standard value 0.7081_4

Age	Author	$Sr^{87}/Sr^{86} \pm 2\sigma$
Quaternary	Present data	$0.7092_3 \pm 0.0002_3$
Tertiary		
Pliocene	Dasch and Biscaye (1971)	$0.7090_0 \pm 0.0001_0$
	Obradovich (1968) in Peterman et al. (1970)	$0.7090_0 \pm 0.0005_0$
Late Miocene	Peterman et al. (1970)	$0.7089_3 \pm 0.0005_0$
Middle Oligocene	do	$0.7081_3 \pm 0.0005_0$
Middle Eocene	do	$0.7078_3 \pm 0.0005_0$
Early Eocene	do	$0.7073_3 \pm 0.0005_0$
Paleocene	do	$0.7074_3 \pm 0.0005_0$
Cretaceous		
Campanian-Maestrichtian	do	$0.7072_3 \pm 0.0005_0$
Albian	Dasch and Biscaye (1971)	$0.7073_0 \pm 0.0001_4$
Barremian-Aptian	Present data	$0.7073_1 \pm 0.0007_0$
Hauterivian	Peterman et al. (1970)	$0.7073_6 \pm 0.0005_0$
Valanginian-Hauterivian	Present data	$(0.7073_2 \pm 0.0009_3)$
Jurassic		
(Oxfordian) Kimmeridgian-Tithonian	do	$(0.7079_8 \pm 0.0003_6)$
Oxfordian	Peterman et al. (1970)	$0.7067_3 \pm 0.0005_0$
Bajocian-Bathonian	Present data	$0.7079_6 \pm 0.0006_4$
Triassic		
Rhaetian	do	$0.7080_2 \pm 0.0004_9$
Norian	do	$0.7072_6 \pm 0.0005_0$
Karnian	Peterman et al. (1970)	$0.7073_3 \pm 0.0005_0$
Ladinian	Present data	$0.7075_1 \pm 0.0006_0$
Anisian	do	$0.7077_2 \pm 0.0005_0$
Werfenian	Peterman et al. (1970)	$0.7080_3 \pm 0.0005_0$
Permian		
Kazanian	Present data	$0.7070_3 \pm 0.0002_1$
Artinskian	do	$0.7073_6 \pm 0.0002_2$
Sakmarian (Wolfkampfian)	Brookins et al. (1969)	$0.7072_3 \pm 0.0006_0$

Continued on next page

Carboniferous		
Stephanian (Virgilian)	Peterman et al. (1970)	$0.7078_3 \pm 0.0005_0$
Westphalian	Present data	$0.7079_9 \pm 0.0003_3$
Visean (Late Missisipian)	Peterman et al. (1970)	$0.7077_3 \pm 0.0005_0$
Tournasian	Present data	$(0.7085_3 \pm 0.0010_0)$
Devonian		
Frasnian-Famenian	Peterman et al. (1970)	$0.7078_3 \pm 0.0005_0$
Eifelian-Givetian	do	$0.7078_3 \pm 0.0005_0$
Emsian	Present data	$0.7084_4 \pm 0.0005_0$
Silurian		
Ludlowian	do	$0.7088_7 \pm 0.0004_0$
Ordovician		
Late Ordovician	Peterman et al. (1970)	$0.7077_3 \pm 0.0005_0$
Middle Ordovician (Llanvirnian-Llandeilian)	Present data	$0.7083_2 \pm 0.0004_0$ $(0.7080_3^2 \pm 0.0006_3)$
Early Ordovician (Arenigian?)	Hedge and Walthall (1963)	$0.7088_3 \pm 0.001$
Cambrian		
Late Cambrian	Present data	$0.7091_4 \pm 0.0007_1$
Middle Cambrian	do	$0.7089_9 \pm 0.0003_5$
Early Cambrian	do	$(0.7095_6 \pm 0.0004_9)$
Precambrian		
Proterozoic		
Adelaidean (570-900? m.y.)		
Wilpena Group		
Wonoka Formation	do	$0.7092_7 \pm 0.0004_6$
Nuccaleena Formation	do	$(0.7095_6^7 \pm 0.0002_5)$
Umberatana Group		
Willochra Subgroup	do	$(0.7097_3 \pm 0.0004_2)$
Trezona Formation	do	$0.7074_2^3 \pm 0.0002_8$
Etina Formation	do	$0.7076_2^2 \pm 0.0002_0$
Brighton Limestone	do	$0.7072_0^2 \pm 0.0003_0$
Burra Group		
Skillogalee Dolomite	do	$(0.7090_5 \pm 0.0004_0)$
River Wakefield Group	do	$(0.7106_0 \pm 0.0002_6)$
Bitter Springs Formation (1000 m.y.?)	do	$0.7068_3 \pm .0002_6$
Bangemall Group (1100 m.y.)		$(0.7083_6 \pm 0.0009_5)$
Belt Series (Newland Lm.) (~1100 m.y.?)	Gast (1960)	$0.7062_3 \pm 0.0020_0$ *

Continued on next page

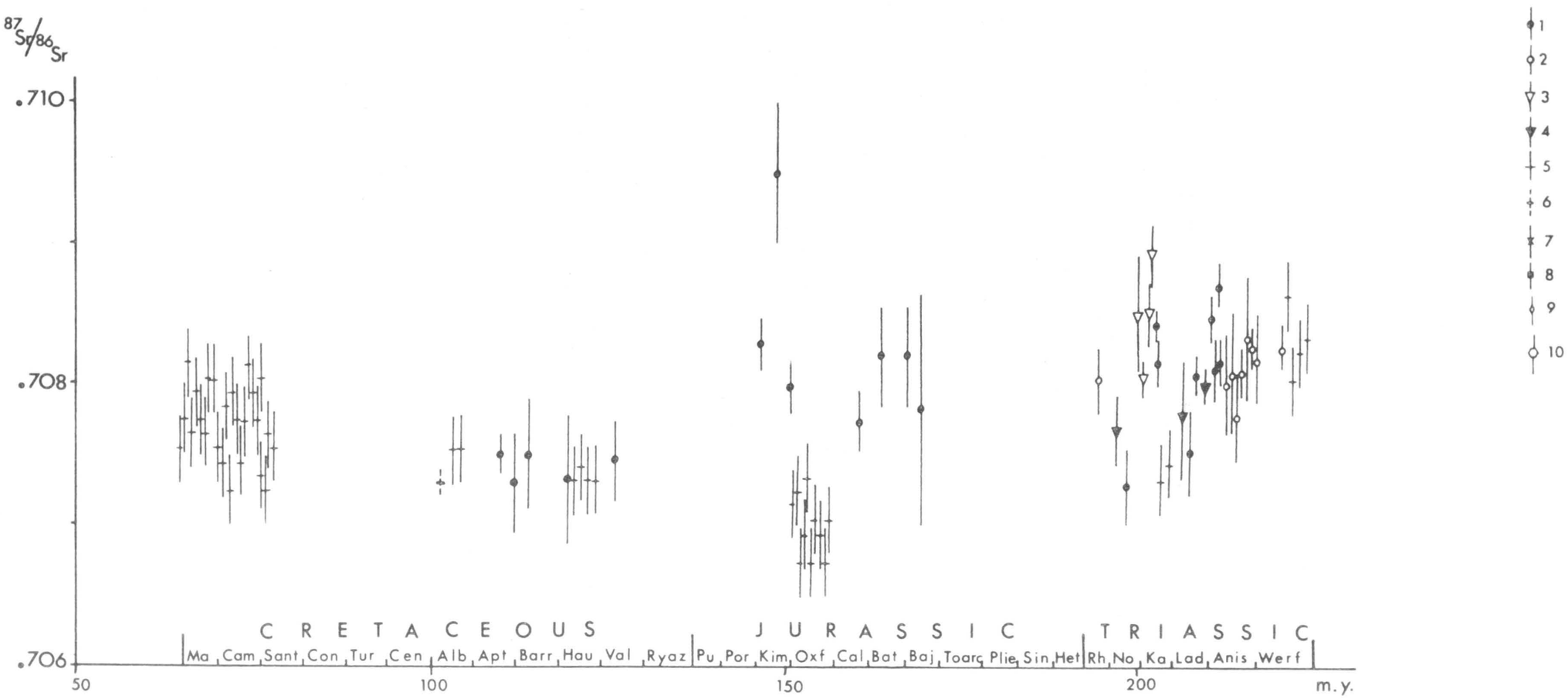
Carpentarian		
McArthur Group (~1500-1600 m.y.)		
Reward Dolomite	Present data	$0.7062_3 \pm 0.0004_6$
Cooley Member	do	$0.7070_8 \pm 0.0004_2$
Mitchell Yard Member	do	$0.7061_6 \pm 0.0004_8$
Mara Dolomite	do	$0.7067_9 \pm 0.0006_5$
Nullaginian		
Mt. Bruce Supergroup (1950-2240 m.y.)		
Wyloo Group		
Duck Creek Dolomite	do	$0.7050_8 \pm 0.0001_9$
Hammersley Group		
Wittenoom Dolomite	do	$(0.7072_3 \pm 0.0004_8)$
Archean		
Superior Province Graywackes (~2500 m.y.)	Hurley et al. (1965)	$0.7014_4 \pm 0.0006_0$
Steep Rock Lake Limestone (~2600 m.y.)	Present data	$0.7019_8 \pm 0.0004_0$
Bulawayan Limestone (~3000 m.y.)	do	$0.7015_1 \pm 0.0002_0$
	Hedge and Walthal (1963)	$0.7015_3 \pm 0.0010_0$ *
	Gast (1960)	$0.7012_3 \pm 0.0020_0$ *
Swaziland System Barites (~3200 m.y.)	Perry et al. (1971)	0.7008_8-0.7017_2 **

** data not normalized to E and A standard value 0.7081_4

* normalization based on the values reported for sea water

The values in parenthesis are suspected to be too high because of their unfavourable Rb/Sr ratios, petrological considerations, signs of recrystallization, or their 2 σ limits are too wide.

Figure 36. Variations of Sr^{87}/Sr^{86} ratios during Mesozoic era.
Explanations:
Present data: (1) limestones (in Triassic open shelf rock types only) (2) limestones of semi-barred basin rock types (Triassic only) (3) early diagenetic dolomites (4) late diagenetic dolomites.
Other measurements: (5) Peterman et al. (1970) (6) Dasch and Biscaye (1971) (7) Brookins et al. (1969) (8) Dasch and Campbell (1970) (9) Hedge and Walthall (1963) (10) Gast (1960).
The vertical bar represents 2σ limits of the mean.



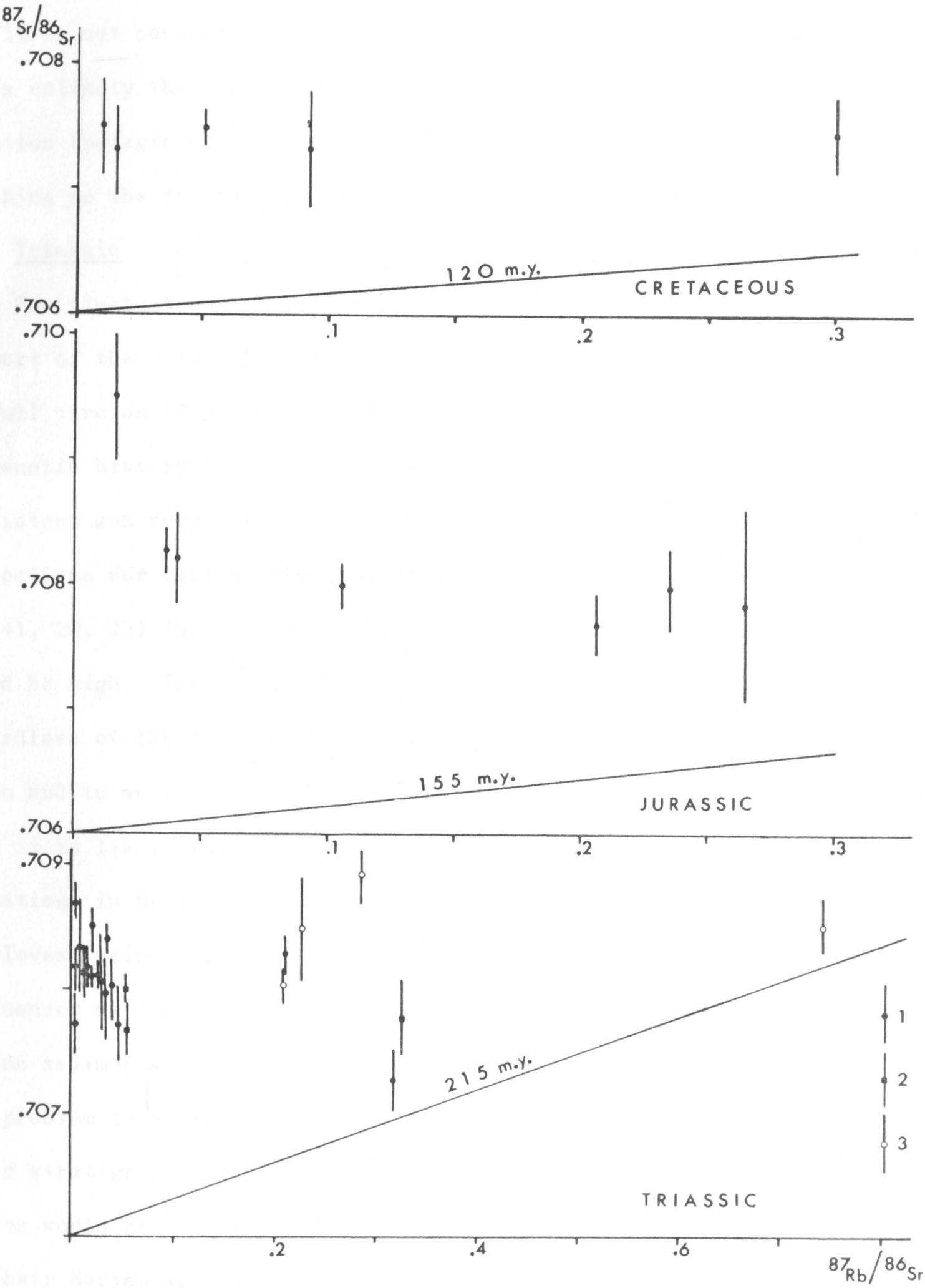


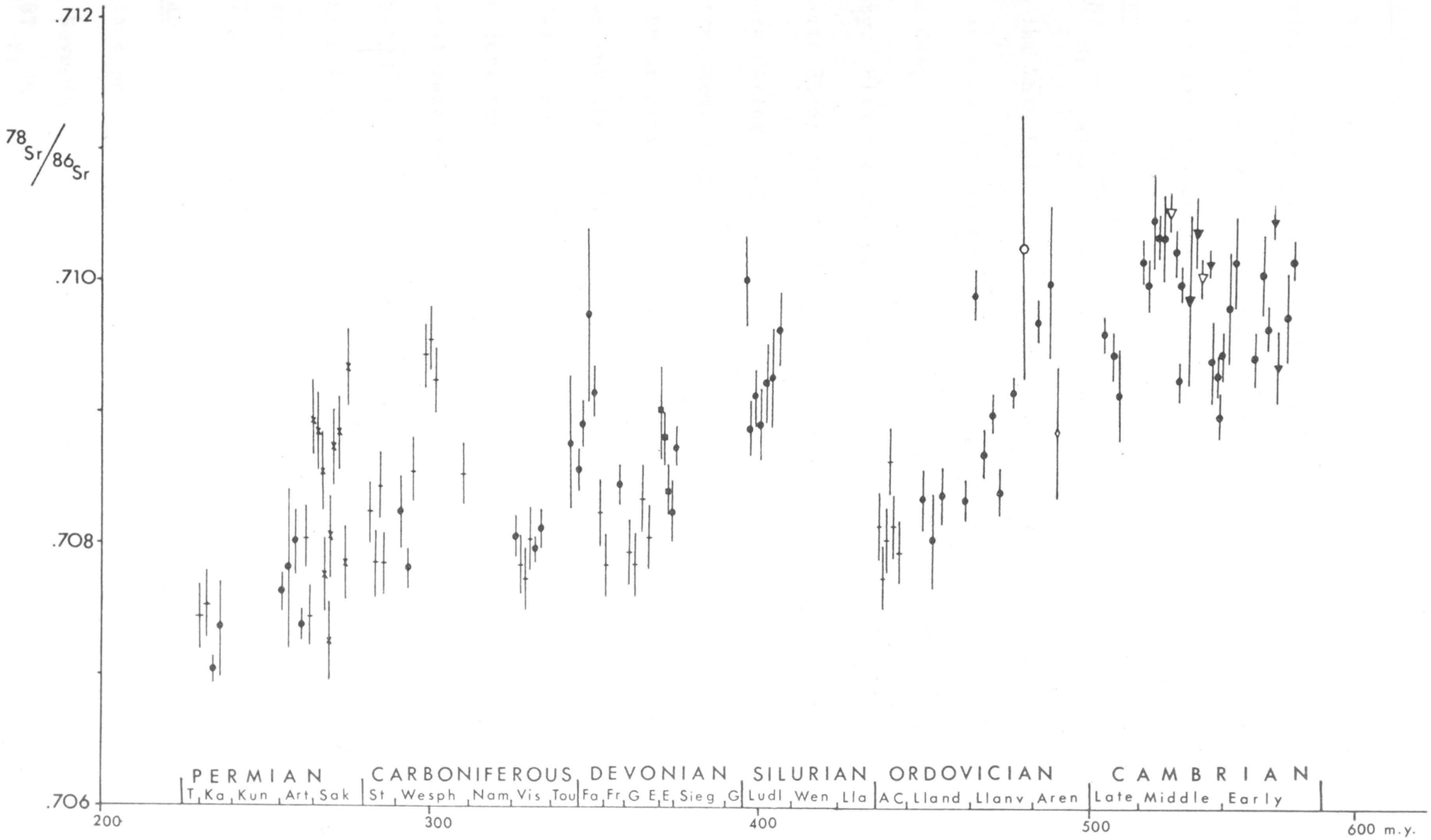
Figure 37. Diagram of the Sr^{87}/Sr^{86} ratios of the leach vs. Rb^{87}/Sr^{86} of the whole rock for the Mesozoic samples.
Explanations: (1) limestones, (2) late diagenetic dolomites, (3) early diagenetic dolomites. The vertical bar represents 2σ limits of the mean. The isochrons are reference lines for the periods considered.

predominantly Kimmeridgian age. Figure 37 shows, that the ratio of sample No. 11 is not consistent with the other data whatever the correction applied. It is unlikely that this represents an original difference in the parent solution (pelagic environment). Epidiagenetic alteration or silicate leaching in the laboratory is a more likely explanation.

Triassic

The fluctuations in Sr^{87}/Sr^{86} ratios have been cited previously in support of the "closed" system diagenetic hypothesis. The samples marked in full circles (fig. 36) formed one hydrodynamic unit during their diagenetic history (cf. Veizer, 1970a), yet the fluctuations with time are consistent and very likely represent a real trend. The maximum age corrections for most of the samples are negligible. In others (Nos. 18, 26, 21, 41, 20, 23) they are below 0.001 and only the correction for sample 22 would be high. The consistency of ratios for different age groups, regardless of the total rock Rb/Sr, points to the low Rb/Sr ratio of the leach and to an insignificant contribution of the radiogenic silicate Sr. Thus it is likely that the variations as indicated by fig. 36 reflect variations in Sr isotopic composition of sea water. The small scatter above the lowest value for each particular age group might be caused by diagenetic influences as discussed previously. The ratios of rocks from semi-barred marine sedimentary environments are within the range of open sea types. The problem is slightly more complicated for the early diagenetic dolomites. Their stratigraphy is uncertain within the Karnian-Norian boundary. Their ratios would be consistent with the Karnian limestone values. In the case of their Norian age even the maximum age correction would not make their ratios compatible (except of 22) with the limestones (No. 18). Accepting their Norian age this would indicate higher Sr^{87}/Sr^{86} of the local sea water or of the "hypersaline" syndiagenetic solutions responsible for the

Figure 38. Variations of Sr^{87}/Sr^{86} ratios during Paleozoic era. Explanations as in figure 36.



sea water or only a secondary phenomenon. Until more data are collected, I am in favour of my values as representative for the whole Wesphalian stage. The Tournasian sample has very wide 2 σ limits and must be accepted only with extreme caution and only as a provisionary value.

The low Rb/Sr ratios of the samples indicates that the possible corrections for age or leaching are negligible.

Devonian

The Sr^{87}/Sr^{86} values of Frasnian and Famenian rocks (fig. 38) are higher than the Late Devonian ratios of Peterman et al. (1970). The data for the Emsian sequence are consistent to within 2 σ limits with the values of Dasch and Campbell (1970) measured on carbonates and apatites from the same locality. With the exception of sample 56, the Sr^{87}/Sr^{86} is correlated positively with Rb/Sr ratio (fig. 39), indicating either partial equilibration of Sr isotopes during diagenesis or leaching of radiogenic Sr during laboratory treatment. It is unlikely that the differences in Sr^{87}/Sr^{86} were caused by original different ratios of sea water, as one would expect higher ratios for the semi-barred Murrumbidgee Series (Nos. 59 and 62) than for the reef-like rocks of the NW Australia in this case. The values observed are just the opposite. The maximum age correction for the sample with the lowest measured Sr^{87}/Sr^{86} ratio, 0.70844, is 0.00022, which is less than the 2 σ limits of a single measurement. Since the samples define a poor isochron (fig. 39), the intercept with Sr^{87}/Sr^{86} axis would indicate an initial ratio $\sim 0.7082_9$. This difference between the two estimates of initial Sr^{87}/Sr^{86} is again less than 2 σ limits of a single measurement.

Silurian

There is a positive correlation between Sr^{87}/Sr^{86} and Rb/Sr values (fig. 39). Nevertheless the correction for the sample with the lowest measured Sr^{87}/Sr^{86} (No. 64, fig. 39) is negligible due to its extremely low

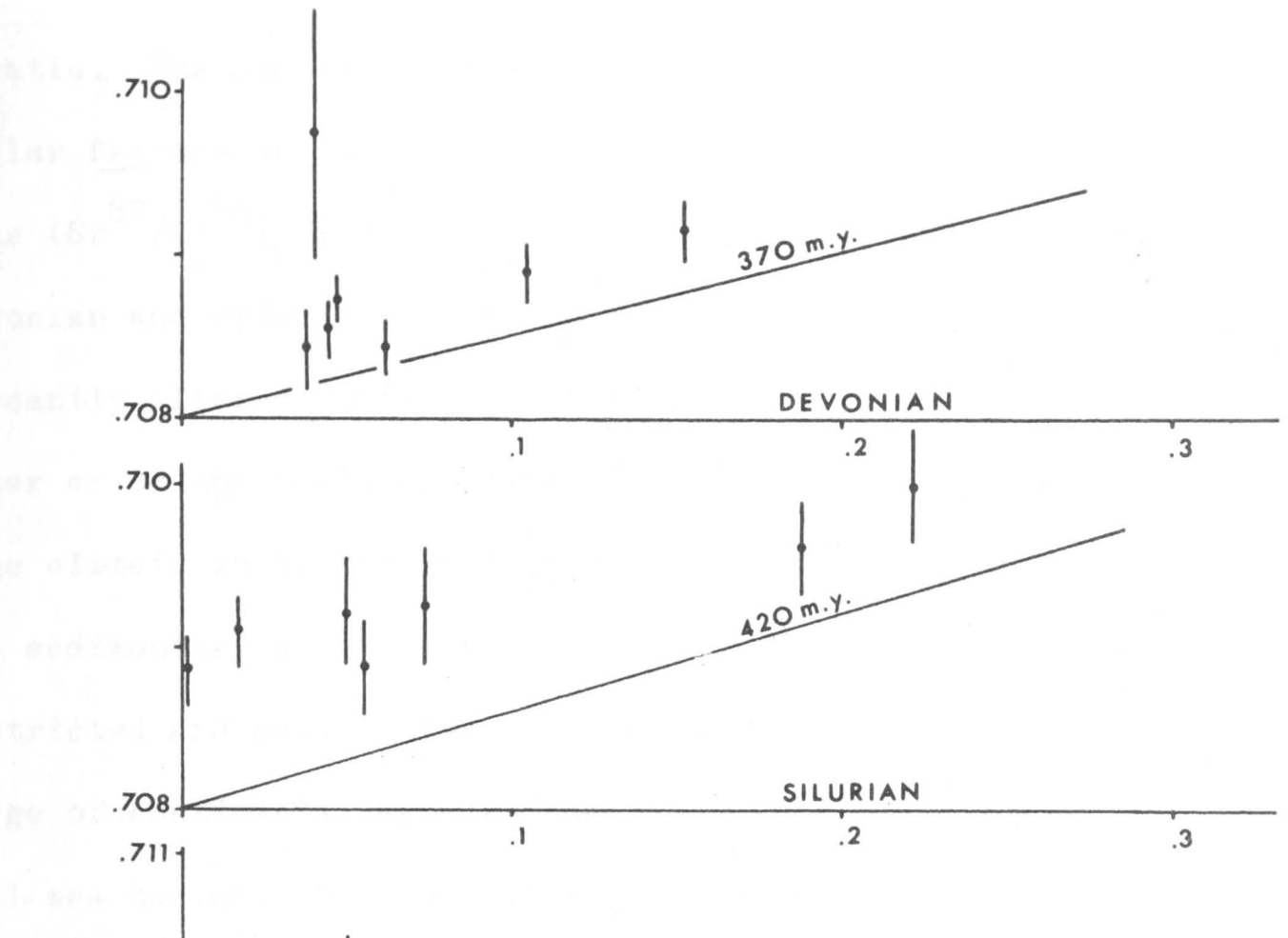


Figure 39. Diagram of the Sr^{87}/Sr^{86} ratios of the leach vs. Rb^{87}/Sr^{86} of the whole rock for the Paleozoic samples. Explanations as in figure 37.

Rb/Sr ratio. The scatter of data around a poor isochron could be explained by similar factors as in the case of Devonian.

The $(Sr^{87}/Sr^{86})_0$ for Silurian (Ludlovian) is higher than the values for Devonian and Ordovician. Assuming that the measured ratio is not significantly altered, this would indicate a higher Sr^{87}/Sr^{86} of the local sea water or of the whole open sea.

The climate in Australia during the Silurian was tropical and humid, and the sedimentary environment of the Hume Series was at least partly semirestricted and euxinic (see Chapter 2). This might lead to a high discharge of continental waters from the Australian Precambrian Shield into marginal sea basins. However, it is very likely that sea water exchange heavily outweighed the continental discharge and also the strong volcanism typical for Silurian of the Yass shelf (cf. Campbell, in Brown et al., 1968) would be possibly more important source of Sr (leaching of tuffs) than the fresh water. From the outlines of general palaeogeography (Campbell, in Brown et al., 1968) one may also conclude that the continental coastline during Silurian period was far to the west of the Yass region.

Summarising the above discussion, the high Sr^{87}/Sr^{86} ratio was probably typical for sea water in general, although the suggestion of a local body of sea water with higher radiogenic Sr content cannot be conclusively rejected.

Ordovician

The Late Ordovician data of Peterman et al. (1970) and the present values are in agreement to within 2 σ limits (fig. 38). The substantial scatter in Middle Ordovician values for Gordon Limestones is probably due to a partial diagenetic equilibration. There are also some problems with precise stratigraphic assignment of the collected samples and it might appear that all Gordon Limestone samples are of Middle Ordovician age

(Colbert, 1970, personal communication). In this case the Middle Ordovician value would be $0.7080_3 \pm 0.0006_3$.

There is no, or only very poor, correlation of Sr^{87}/Sr^{86} with Rb/Sr (fig. 39) and thus it is unlikely that the best values are considerably altered.

Cambrian

Lack of correlation between Sr^{87}/Sr^{86} and Rb/Sr for Cambrian samples (fig. 39) would indicate only small possible corrections of the best values. The maximum age correction for the lowest Sr^{87}/Sr^{86} would be only 0.00052.

The preferred Sr^{87}/Sr^{86} values are higher for Cambrian than for any previous period with well established Sr isotopic ratio (fig. 38). Whether this is a primary or secondary phenomenon is difficult to judge. Deans et al. (1966) and Powell et al. (in Powell, 1966) reported values as low as 0.7083 for Late Cambrian Ottertail Limestones of British Columbia, and Gittins et al. (1969) reported 0.7077 for (Middle?) Cambrian Durness Limestones of Scotland. Since both suites are very strongly metamorphosed by alkaline complexes, the data must be accepted only with caution. In the absence of better defined data, the values presented in Table 9 are accepted as representative of the Cambrian period.

If true, the Cambrian would be a period of the highest Sr^{87}/Sr^{86} ratio of sea water during the whole Phanerozoic (and possibly the whole geologic) history of the Earth. However, the Cambrian rocks are mainly intertidal and shallow subtidal sediments peripheral to the old Precambrian shield, and so the possibility of a higher content of radiogenic Sr in water of such basins must be kept in mind.

Precambrian

Proterozoic

Adelaidean

Sr^{87}/Sr^{86} values selected for the time interval 570-900? m.y. are summarized in Table 9 and fig. 40. The values in parenthesis are considered to be too high because of their unfavourable Rb/Sr ratios, petrological considerations, as well as their high age.

The problem of possible exchange of Sr between carbonate and silicate phases has been discussed in the introductory part of this chapter. It is well illustrated by the rocks of this time interval. Assuming that all Rb and Sr is concentrated in the carbonate fraction of the rock, and calculating the $(Sr^{87}/Sr^{86})_0$, it is clear that even such a maximum age correction would not bring the values of samples 145, 131, 132, 138, 139 and 140 down to the ratios indicated by other contemporaneous samples (fig. 41). This is so also for the samples 11 (Jurassic), 74, 77, 79 and possibly 80, 81 (Ordovician) and probably some Triassic rocks. The samples at present very likely have higher Rb/Sr ratios than early in their history, since diagenetic influences cause loss of Sr compared to Rb. Thus their high Sr^{87}/Sr^{86} cannot be attributed to an initially higher Rb/Sr ratio.

We must be dealing therefore with a mixed Sr^{87}/Sr^{86} from at least two end members with different Sr isotopic and Rb/Sr proportions (carbonate and silicate phases).

Whether the high values in the leach are due to simple leaching of radiogenic Sr from the silicate phases or to a partial equilibration between carbonate and silicate cannot be distinguished clearly from the present data. In my view the much higher solubility of carbonate Sr compared to the silicate Sr (cf. p. 99), the lack of distinctive correlation between Sr^{87}/Sr^{86} and Rb/Sr in similar petrological types, the common signs of recrystallization and strong diagenesis accompanied by loss of part of the carbonate Sr, indicate some degree of partial equilibration during deep

Figure 40. Variations of Sr^{87}/Sr^{86} ratios during younger Proterozoic era.
Explanations: (1) limestones, (2) early diagenetic dolomites, (3) siltstones, (4) silicites, (5) Gast (1960).
The vertical bar represents 2σ limits of the mean.

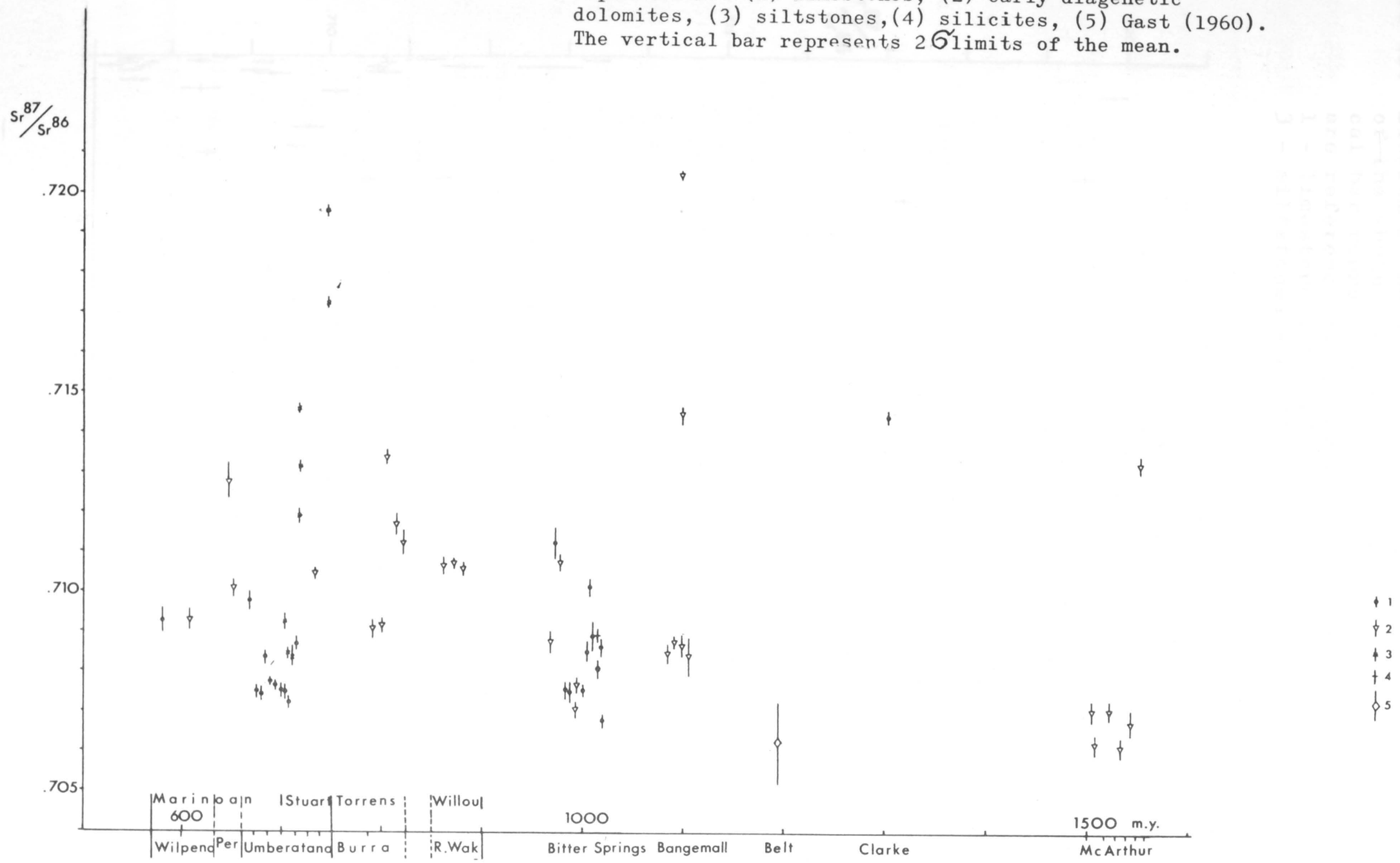
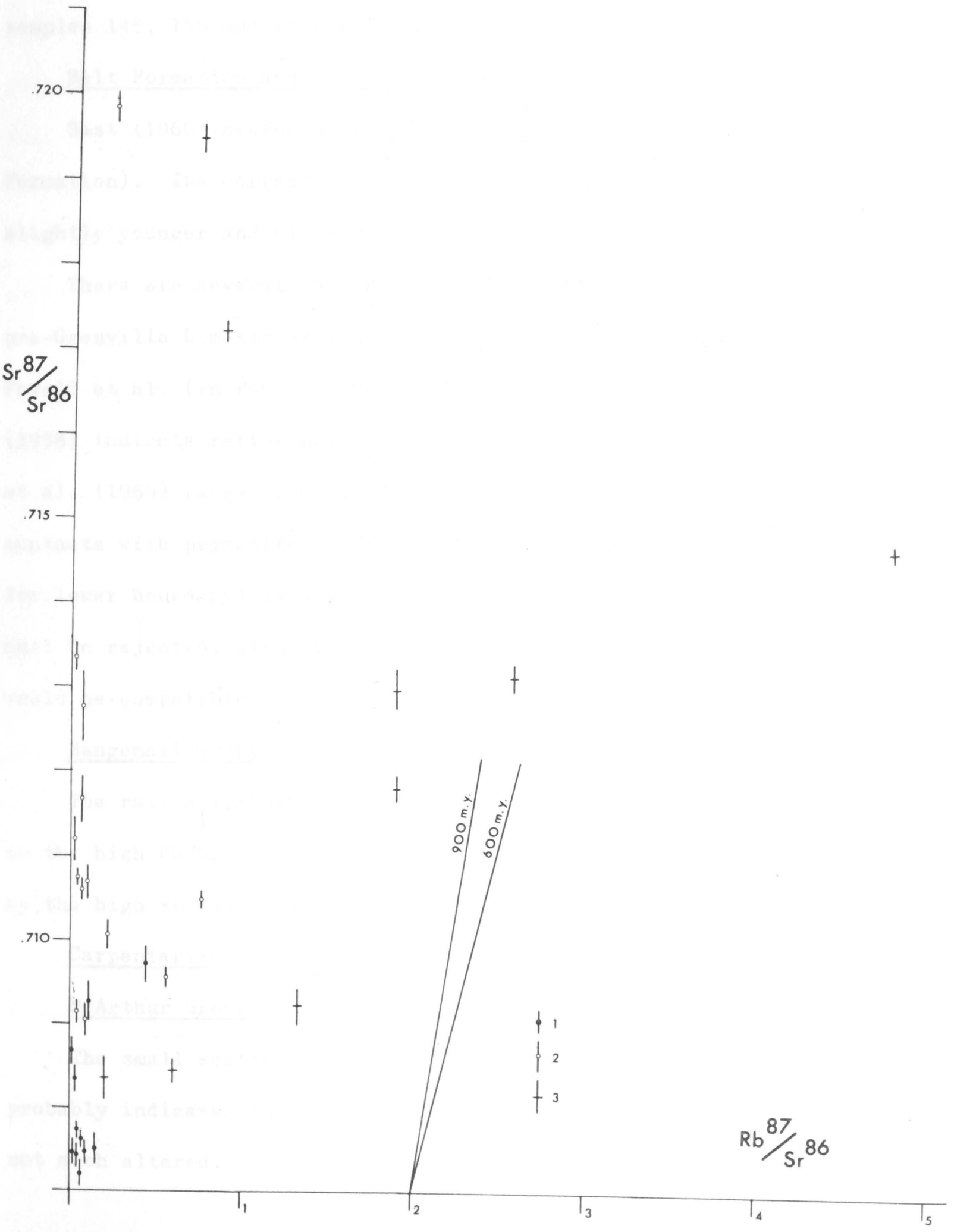


Figure 41. Diagram of the Sr^{87}/Sr^{86} ratios of the leach vs. Rb^{87}/Sr^{86} of the whole rock for the Adelaidean samples. The vertical bar represents 2σ limits of the mean. The isochrons are reference lines for the Adelaidean System.
1 - limestones, 2 - early diagenetic dolomites,
3 - siltstones and silicites



burial anadiagenesis and epidiagenesis.

Bitter Springs Formation

The selected value (0.7068_3) is very likely a good approximation to the contemporaneous sea water composition. The explanation of the high radiogenic Sr content of the Adelaidean rocks is applicable also to the samples 148, 156 and possibly 158, 159 and 151.

Belt Formation and Grenville Limestones

Gast (1960) measured Sr^{87}/Sr^{86} ratio of the Newland Limestone (Belt Formation). The corrected value is in good agreement with the ratios of slightly younger and older rocks.

There are several measurements of Sr isotopic ratios in Grenville and pre-Grenville Limestones and Marbles. The corrected data of Gast (1960), Powell et al. (in Powell, 1966), Hedge and Walthall (1963) and Pinson et al. (1958) indicate ratios between 0.706 and 0.708. However the data of Gittins et al. (1969) range from 0.702 to 0.709 in marbles and hybrid rocks on the contacts with pegmatites. Due to the uncertainty in age (no definite limit for lower boundary) as well as very strong magmatic alteration these ratios must be rejected, although the values published by the first group of authors would be compatible with my data.

Bangemall Group

The ratios measured for this suite of rocks are probably too high due to the high Rb/Sr ratios and partial diagenetic equilibration, as indicated by the high spread of data (168, 167, 165) (fig. 40).

Carpentarian

McArthur Group

The small scatter in Sr^{87}/Sr^{86} ratios (except of 175) (fig. 40) probably indicates that the original Sr isotopic composition of rocks is not much altered.

Nullaginian

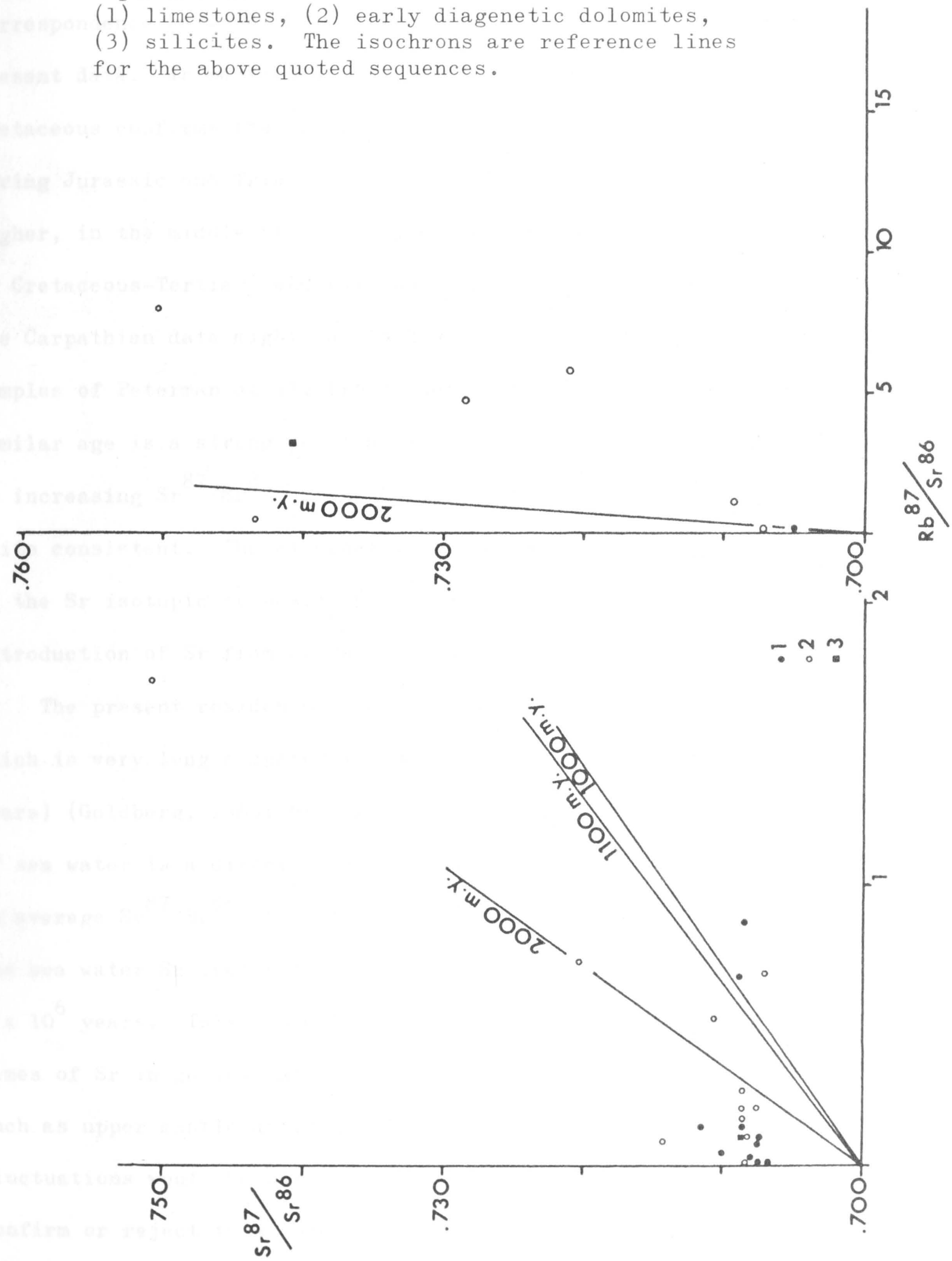
Mt. Bruce Supergroup

The wide spread of both Rb/Sr and Sr^{87}/Sr^{86} ratios (Appendix 1 and fig. 42), the evidence of strong diagenetic (partly open system) alteration, resulting in the loss of Sr, and very unfavourable Rb/Sr ratios do not permit any firm conclusion. The selected value of Duck Creek Dolomite seems to be consistent with the general trend of Sr^{87}/Sr^{86} for Proterozoic rocks (fig. 43), but due to the above difficulties additional analysis would be required. The maximum age correction for its present Rb/Sr ratio would be 0.0006_4. Even after this correction the value would be consistent with the above general trend. This conclusion would not be valid in the case of a very strong equilibration with a silicate phase with high initial radiogenic Sr. On the basis of K/Al and K/Rb data it was concluded that the original silicate phase might have been derived from basic volcanics (p. 46). If this interpretation is valid, the $(Sr^{87}/Sr^{86})_0$ of the silicate phase was probably between 0.702-0.706 and this might add some weight to the validity of the selected value ($0.7050_8 \pm 0.001_9$).

Archaean

Both Steep Rock Lake and the Bulawayan Limestones have very low Rb/Sr ratios and the estimates of $(Sr^{87}/Sr^{86})_0$ are quite precise. There is excellent agreement between the present data and the corrected data of Gast (1960) and Hedge and Walthall (1963) for the Bulawayan Limestones. The best value of Hamilton and Deans (1963) is also in agreement for Bulawayan Limestone, but I was not able to establish with certainty the Eimer and Amend standard value for their laboratory.

Figure 42. Diagram of the Sr^{87}/Sr^{86} ratios of the leach vs. Rb^{87}/Sr^{86} of the whole rock for the Bitter Springs Formation and Bagemall Group (left) and the Mt. Bruce Supergroup (right) rocks.
Explanations:
(1) limestones, (2) early diagenetic dolomites, (3) silicites. The isochrons are reference lines for the above quoted sequences.

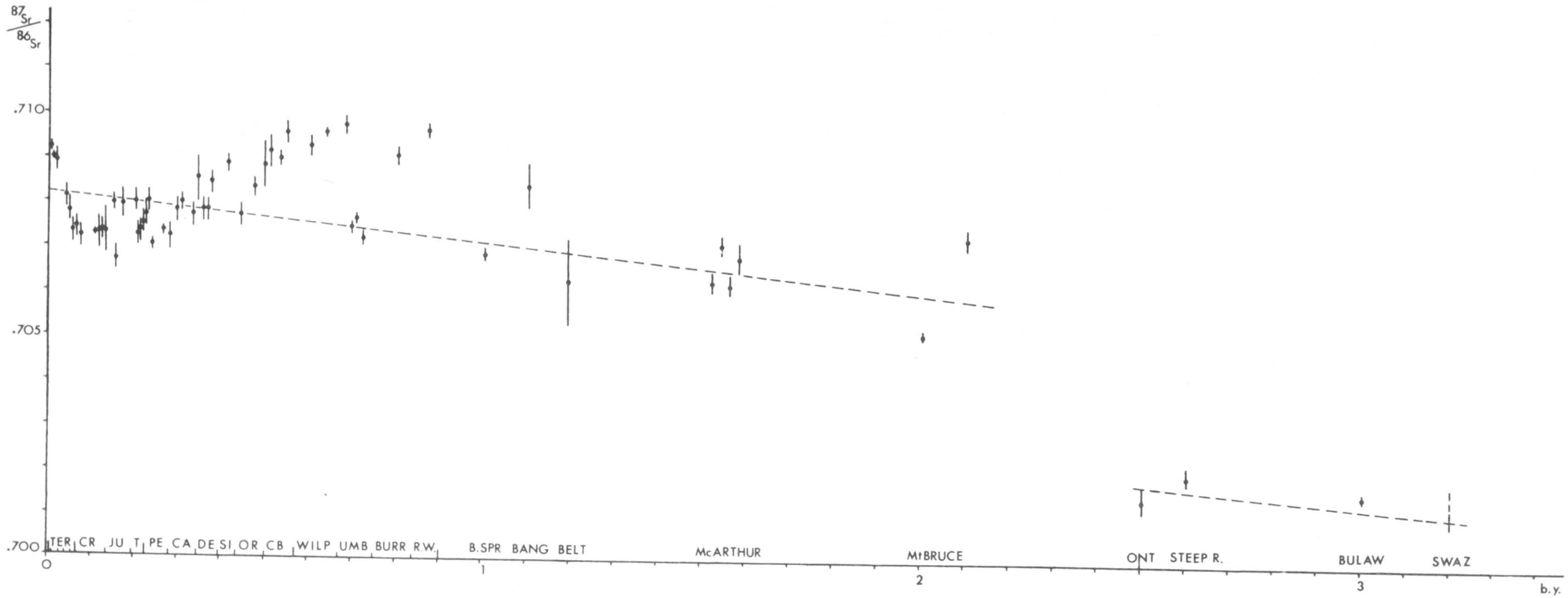


10.6 Sr^{87}/Sr^{86} VARIATIONS IN SEA WATER DURING GEOLOGIC HISTORY

Selected values of Sr^{87}/Sr^{86} are summarised in fig. 43. There is some correspondence between the variations of Peterman et al. (1970) and the present data. In particular, the agreement in low values for Early Cretaceous confirms the previous data. The situation is more complicated during Jurassic and Triassic periods. All European samples cluster somewhat higher, in the middle of the "depression" formed by two ascending trends of Cretaceous-Tertiary and Paleozoic ages (fig. 43). This indicates that the Carpathian data might be too high, but the agreement between the Karnian samples of Peterman et al. from Siberia and the Carpathian samples of similar age is a strong point against such an interpretation. The trend of increasing Sr^{87}/Sr^{86} during Norian-Werfenian stages also seems to be quite consistent. The alternative explanation is a real but rapid change in the Sr isotopic composition of sea water, possibly achieved by the introduction of Sr from different sources (Faure et al., 1965).

The present residence time of Sr in sea water is $\sim 20 \times 10^6$ years, which is very long compared to the mixing rate of the ocean water ($\sim$1000 years) (Goldberg, 1963; Broecker, 1963). The isotopically well-mixed Sr of sea water is a direct reflection of this situation. Assuming 0.712 as an average Sr^{87}/Sr^{86} of continental waters, the time required to change the sea water Sr isotopic ratio from 0.708 to 0.709 would be about 5×10^6 years. This would be valid only in the case of similar residence times of Sr in geological past and disregarding all other sources of Sr, such as upper mantle derived volcanics. Nevertheless in theory rapid fluctuations would be possible. The present data are not sufficient to confirm or reject this inference. Similarly the data are not sufficient to rule out a possibility of higher Sr^{87}/Sr^{86} ratios of the vast semi-barred epicontinental seas of the geological past.

Figure 43. Plot of selected Sr^{87}/Sr^{86} ratios of sea water vs. geological time. The vertical bar represents 2σ limits of the means. The dashed lines are calculated least square fit regression lines for the Alternative 1.

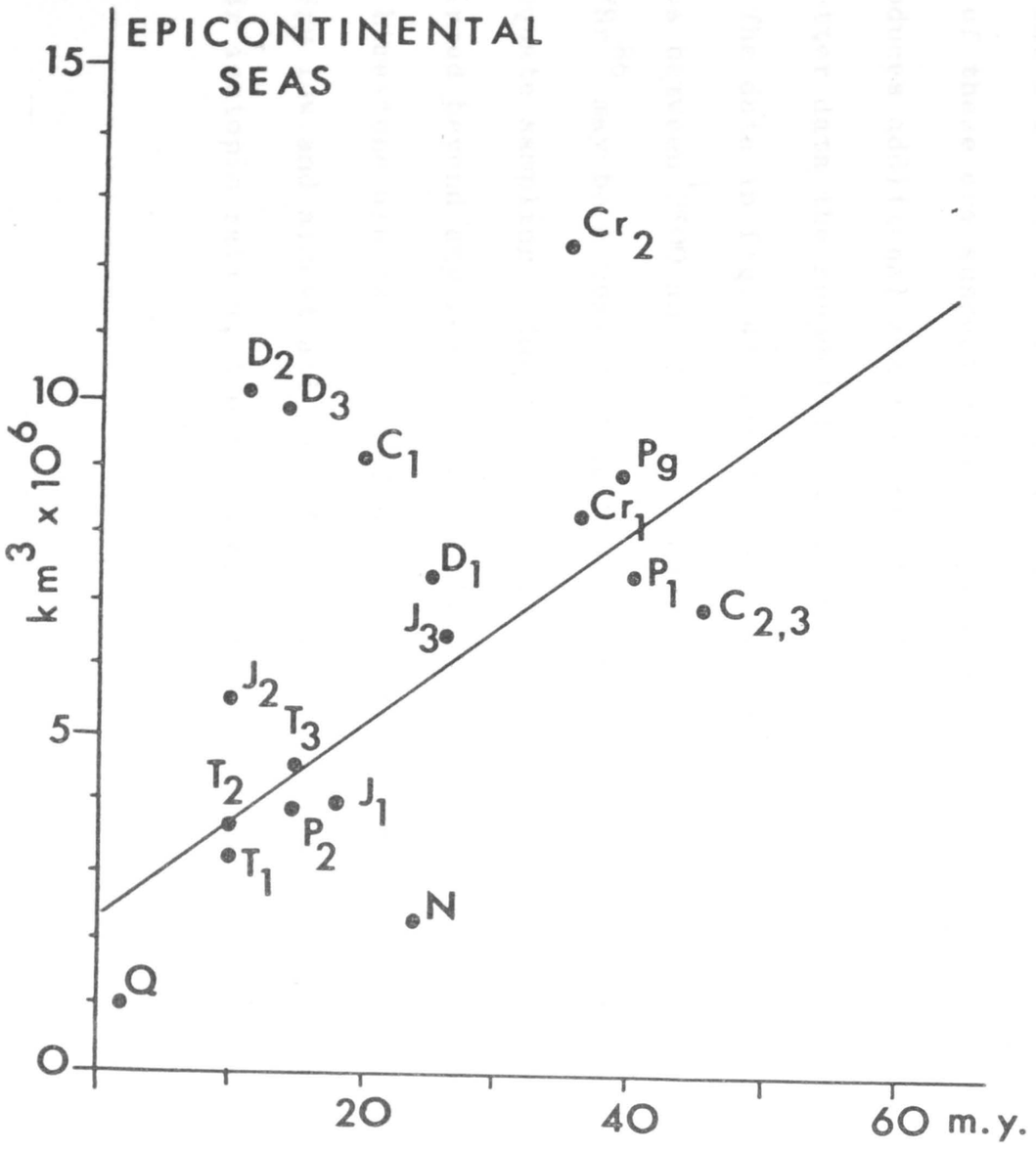


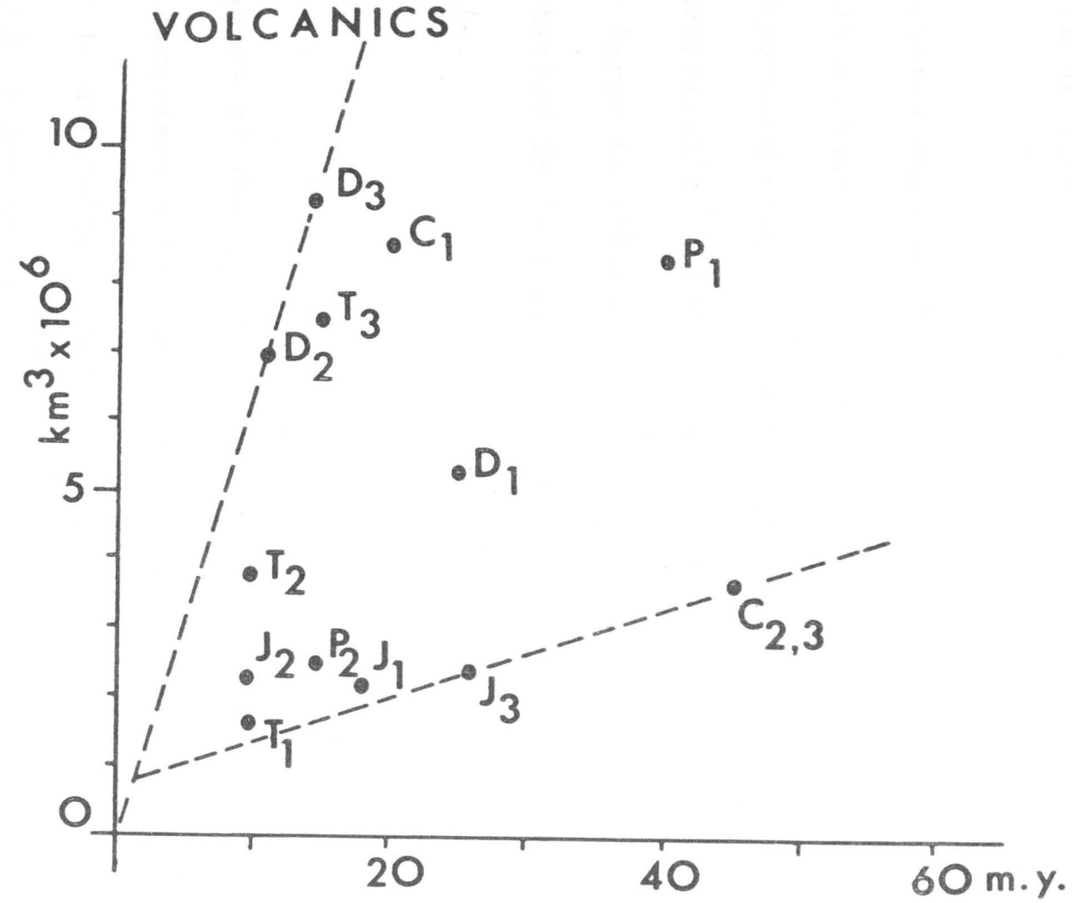
Because of the above discussed difficulties as well as the problems created by diagenesis (p. 109), the Triassic peak of Peterman et al. would require additional confirmation. In any case, even if confirmed, the peak is rather of Early than of Late Triassic age. The second peak (Pennsylvanian) was not confirmed by the present data. The high values for Cambrian, Ordovician and Silurian are very uncertain and need further confirmation. There are some indications (p.118) that the measured values might be too high.

Summarising the above discussion, the data in their present state are not sufficient to substantiate speculations on their correlation with tectonic events (Peterman et al., 1970) or glacial erosion (Armstrong, 1971a). Unless the rapid fluctuations in Sr isotopic composition of sea water are confirmed, the lack of the Pennsylvanian peak disallows both previously advanced explanations.

The data of Ronov (1959, 1968), Egyed (1956) and others on the extent of volcanic activity, the volume of epicontinental seas and volume of carbonate deposition etc. for various geological periods are not normalised to time. When normalisation is done (Veizer, 1971) a strong positive correlation is revealed between the length of the time interval and the above quoted variables. This correlation is even more obvious for more recent data (fig. 44). After normalisation, it is clear that the Triassic is no more "geocratic" a period than most of the others. So the Triassic peak, even if confirmed, cannot be correlated with a period of high exposure of continental shields to erosion. Similarly the Jurassic does not seem to be a period of extensive volcanicity. Calculations of Garrels and MacKenzie (1971b) indicate a denudation rate 120 x 10^{14} g/year for Pleistocene, 75 x 10^{14} for Carboniferous, Mesozoic and Tertiary and 300 x 10^{14} for uppermost Precambrian to Devonian. There is a rough

Figure 44. Plots of the volume of epicontinental seas and volume of volcanics vs. the lengths of the time intervals represented by each particular period. The diagrams are based on the values published by Ronov (1968).
Explanations: D - Devonian, C - Carboniferous, P - Permian, T - Triassic, J - Jurassic, Cr - Cretaceous, Pg - Paleogene, N - Neogene, Q - Quaternary.


EPICONTINENTAL SEAS
15
10
5
0
km3 x 10^6
Cr2
D2
D3
C1
Pg
Cr1
D1
P1
C2,3
J3
J2
T3
T2
J1
P2
T1
N
Q
20
40
60 m.y.


VOLCANICS
10
5
0
km3 x 10^6
D3
C1
P1
T3
D2
D1
T2
J2
P2
J1
J3
T1
C2,3
20
40
60 m.y.

correspondence between these denudation data and Sr isotopic values, but the uncertainty in Sr isotopic composition of Early Paleozoic sea water is high.

All previously quoted examples have taken only the evolution of continental crust into account. The influence of oceanic crust and volcanism were not discussed owing to the lack of pre-Cretaceous data. Nevertheless, the uncertainties involved using only crustal evolution are already sufficiently large to illustrate the futility of speculation on the causes of the detailed Sr isotopic fluctuations of sea water, at least in their present state.

10.7 DISCUSSION

Although the causes of the detailed fluctuation of Sr^{87}/Sr^{86} ratios of sea water cannot be discussed with confidence in their present state, it might be of interest to define the general trend as indicated by the ratios in carbonate rocks and to discuss its possible causes.

The selected data as summarized in Table 9 are plotted in figure 43. Some of these are suspected to be too high (cf. Table 9) and if so this introduces additional scatter into the trend. Nevertheless in the absence of better data the suspected values were not rejected.

The data in fig. 43 seem to indicate an offset of sea water Sr isotopic ratios between 2500 and 2100 m.y. ago. This sudden increase of sea water Sr^{87}/Sr^{86} may be a real feature or only an apparent trend due to the inadequate sampling. The value for the Bulawayan Limestone seems to be confirmed beyond any reasonable doubt. The two values for the Steep Rock Lake Limestone are identical within 2 σ limits. Since their Rb/Sr ratio is very low and almost all secondary influences (cf. p. 112) would increase the Sr isotopic ratios, the measured data may be regarded as valid. The

value for the Wyloo Group (0.705) is probably a close approximation to the contemporaneous sea water ratio, but the chance of secondary alteration cannot be rejected conclusively. The close grouping for the McArthur Group indicates that those ratios are very likely original sea water values. Thus even if the Mt. Bruce Supergroup (Wyloo Group) data are rejected, the increase between approximately 2500 and 1650 m.y. would be higher than for the preceding and succeeding periods. This would indicate that the offset is a real feature and not a trend caused by inadequate sampling.

Supporting evidence which indicates the presence of a geologically-important event around the Archean-Proterozoic boundary may be summarized as follows:

(a) The majority of geochemical trends described in Chapter 8 indicate changes of trends at about this time interval. This is particularly clear in the K/Rb ratio diagram (fig. 26), which indicates similar offset of values.

(b) From the evaluation of tectonics in Earth history (Nature, 1971, Anhaeusser et al., 1969; Martin, 1969) it seems that the tectonics of "greenstone belts" was superseded by "geosynclinal" tectonics at about 3.0 to 2.5 b.y. ago.

(c) Archean sequences contain a high proportion of graywackes, whereas the Proterozoic sequences are characterised by high abundances of arkoses (Ronov, 1964). Since those immature detrital rocks reflect directly the composition of the source region, one has to postulate a more mafic composition of the upper continental crust in Archean and presence of widespread granitic plutons in Proterozoic.

(d) According to Muehlberger et al. (1967) at least 50% of the North American basement was already in existence 2500 m.y. ago. Ronov (1964) speaks about formation of 60% of present day granites at this time interval,

although such high proportions were not confirmed by Hurley and Rand (1969).

(e) A strong phase of crustal fractionation at about 3 b.y. ago was postulated also on the basis of Rb-Sr and Ph-U-Th isotopic data by Slawson et al. (1963), Patterson and Tatsumoto (1964) and Armstrong (1968).

Thus, although the arguments are not conclusive, they seem to indicate a geological "event(s)" of global importance in the Late Archean. Therefore the offset of Sr isotopic values will be accepted as real and the Sr isotopic trends for Archean and Proterozoic + Phanerozoic will be considered separately.

The least square linear regression lines for Archean and Proterozoic + Phanerozoic, calculated on the basis of data in Table 9, are plotted in fig. 43. These two least square lines together with their connecting line between 2.1 and 2.5 b.y. will be referred to as Alternative 1. Probably more realistic approximation to the sea water evolutionary trend is obtained by connecting the present day sea water ratio (0.7092) with the ratio for the Wyloo Group (0.7051). This will exclude the influence of the suspected high values. It would be also feasible to exclude the data of Perry et al. and Hurley et al. for the Archean, since their measurements were made on sedimentary barites and graywackes. Such corrected trends and their connection will be referred to as Alternative 2.

Accepting the role of the ocean as a transient system for elements introduced by continental discharge and their later removal by sedimentation (cf. Garrels and MacKenzie, 1971a, chapter 11) one would expect the sea water Sr isotopic ratios to resemble the evolutionary curve of the continental crust (although Sr from the mantle is also an important component). This statement might be supported by the rough correlation of the denudation data and Sr isotopic values for the Phanerozoic (p. 123).

Therefore it is of interest to find possible crustal evolutionary models which would resemble the Sr isotopic data of sea water.

The models would have to satisfy the following constraints (see also the references in Armstrong, 1968, table 3):

(a) Sr^{87}/Sr^{86} of the primordial Earth was 0.698-0.699 (Gast, 1960; Papanastassiou and Wasserburg, 1969 and references in Armstrong, 1968).

(b) Present day Sr^{87}/Sr^{86} ratio of the upper mantle is between 0.702 and 0.704 and its present day Rb/Sr ratio is about 0.010 (Armstrong, 1968; Hurley and Rand, 1969; Hart and Brooks, 1970; Wasserburg, 1964 and others).

(c) The average present day Rb/Sr ratio of the continental crust is about 0.150 (Hurley, 1968; Armstrong, 1968; Hurley and Rand, 1969). It is difficult to establish the average present day Sr^{87}/Sr^{86} of the continental crust. The estimates vary from 0.720 for the old Precambrian regions (Faure et al., 1963) to about 0.710 for recently formed "new" crust (Hurley and Rand, 1969). The summary in Table 8 indicates 0.7154 as a possible average value for the present day continental crust. This estimate or somewhat lower value might be tentatively accepted as the average present day Sr^{87}/Sr^{86} ratio of the continental crust.

It has been shown already by Armstrong (1968) that instantaneous fractionation into felsic crust and mafic upper mantle at about 4.6 b.y. ago would lead to Sr^{87}/Sr^{86} values for the crust which are too high and ratios for the mantle which are too low (cf. C_f and M_f in fig. 45).

Hurley et al. (1962) postulated a continuous process of crustal formation from the mantle. The mantle may be regarded as an infinite reservoir (Hedge, 1966), or a finite reservoir which is successively depleted in both Rb and Sr either by multistage evolution (Hurley, 1968) or by a continuous transport model (Hart and Brooks, 1970). Measurements of the Sr^{87}/Sr^{86} of Archean volcanics (Hart and Brooks, 1970) can be

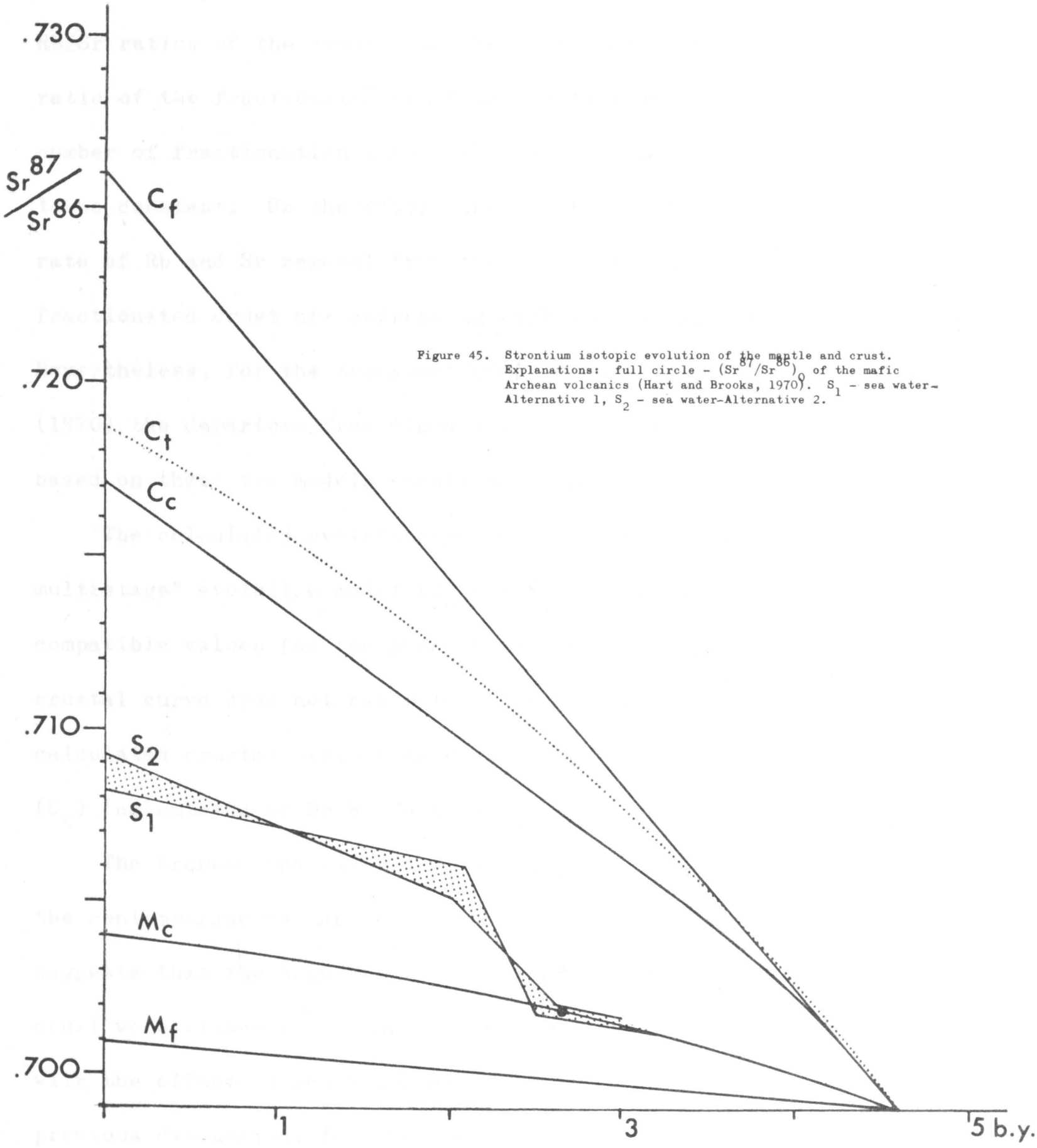


Figure 45. Strontium isotopic evolution of the mantle and crust. Explanations: full circle - $(Sr^{87}/Sr^{86})_0$ of the mafic Archean volcanics (Hart and Brooks, 1970). S_1 - sea water-Alternative 1, S_2 - sea water-Alternative 2.

consistent with a two stage, multistage or continuous transport model, if the Earth's crust formed continually, and would not support the infinite reservoir model. The multistage evolution and continuous transport models differ mainly in the rate of Rb and Sr removal from the mantle and in the Rb/Sr ratios of the crust. In the multistage evolution model the Rb/Sr ratio of the fractionated crust is constant and in the case of an infinite number of fractionation stages the rate of fractionation is also assumed to be constant. On the other hand, in the continuous transport model the rate of Rb and Sr removal from the mantle and Rb/Sr ratio of the fractionated crust are decreasing with increasing depletion of the mantle. Nevertheless, for the transport coefficients calculated by Hart and Brooks (1970) the departure from linearity is not very large and so the conclusions based on these two models should be comparable.

The calculated evolutionary curves (Appendix 4) for the "infinite multistage" evolution model (C_c and M_c in fig. 45) indicate almost compatible values for the present day crust and upper mantle, but the crustal curve does not resemble the sea water curve. Similarly the calculated crustal evolutionary curve for the continuous transport model (C_t) (calculated by Dr W. Compston) does not resemble the sea water data.

The Archean sea water data are identical with Sr isotopic values for the contemporaneous mantle derived volcanics (Hart and Brooks, 1970), which suggests that the high Rb/Sr phases of the contemporaneous continental crust were either very young or their proportion was very small. Together with the offset in sea water data and other indications summarised in the previous discussion, this in turn suggests the occurrence of a strong crustal fractionation phase in the Late Archean, say at about 3.0 b.y. ago. Prior to this period the crust and mantle were only little differentiated. This does not necessarily mean the instantaneous fractionation of, say 50%

of the present continental crust at 3.0 b.y. ago, but rather that the fractionation rate between about 3.5 and 2.5 b.y. was several times faster than during younger periods.

The model in which the crust and mantle were essentially undifferentiated during the first 1.5 b.y. of the Earth history is presented in figure 46. In the case of complete instantaneous fractionation of the continental crust at about 3.0 b.y. ago (C_f and M_f), the value for the present day crust is probably too high and the agreement with sea water values is poor.

Assuming the "infinite multistage" evolution model since 3.0 b.y. ago, the agreement between sea water data and crust is much better, but the value for the present day upper mantle is too high (fig. 46, C_c and M_c).

In order to reduce the upper mantle Sr isotopic ratios, it is necessary to initiate a higher loss of Rb in the early fractionation stages. Assuming formation of 50% of present day continental crust at about 3.0 b.y. ago and continuous fractionation of the remaining 50% during younger periods of the Earth evolution, evolutionary curves could be found which could satisfy all constraints and could also explain the steep rise of sea water values in Early Proterozoic (fig. 47, C_c50, M_c50). Since this model, as well as the continuous transport model both require higher Rb and Sr removal from the mantle in the early fractionation stages, the close agreement between the two calculated crustal curves (C_c50 and C_t) (C_t calculated by Dr W. Compston) is not surprising. This is probably as good a fit as can be obtained by utilising simple fractionation models of the crust.

Essentially similar conclusions would be reached utilising the infinite reservoir model. The calculated crustal curves for the "infinite multistage" evolutionary model and infinite reservoir model would not be

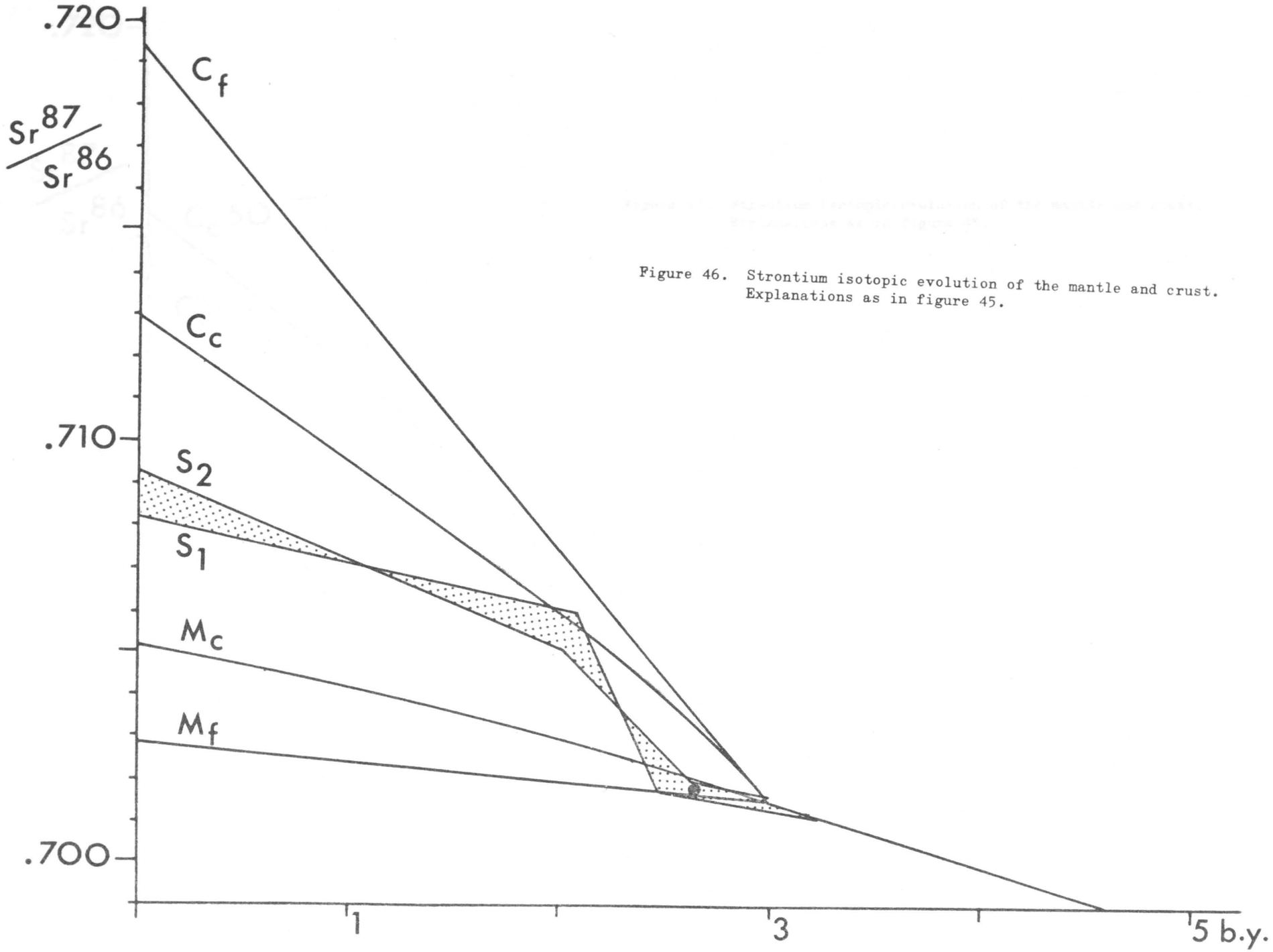


Figure 46. Strontium isotopic evolution of the mantle and crust. Explanations as in figure 45.

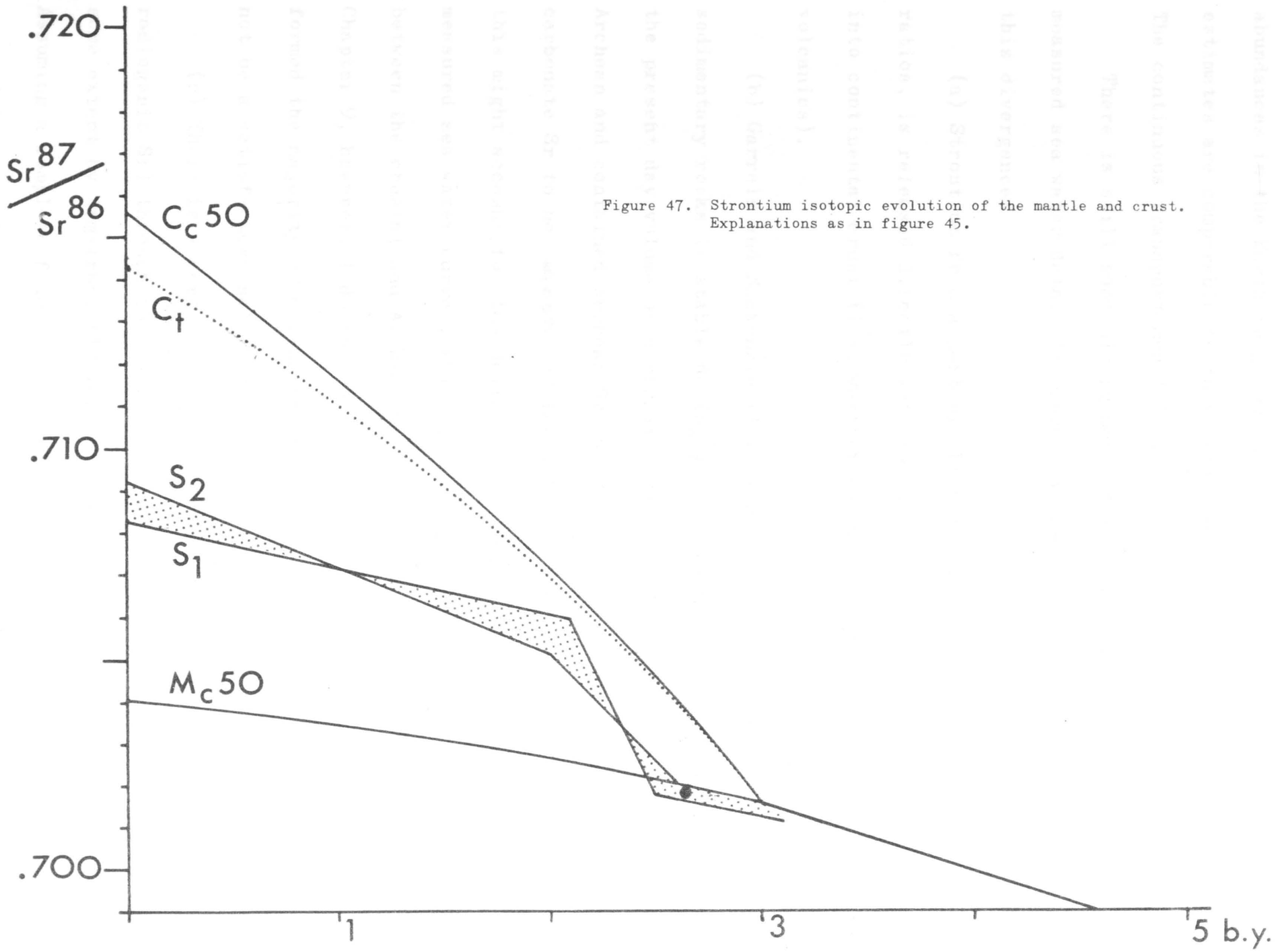


Figure 47. Strontium isotopic evolution of the mantle and crust. Explanations as in figure 45.

appreciably changed even accepting different estimates of Rb and Sr abundances in the Earth (e.g. Hurley, 1968), providing the crustal estimates are comparable to those utilised in the present calculations. The continuous transport model is independent of these estimates.

There is still some divergence between the calculated crustal and measured sea water data. At present I see three possible explanations of this divergence:

(a) Strontium from a part of the mantle, which has low Sr^{87}/Sr^{86} ratios, is released directly into sea water, without being incorporated into continental crust (i.e. weathering of the ridge or island arc volcanics).

(b) Garrels and MacKenzie (1971a) believe that the volume of sedimentary rocks is stable during geological history and, if this is true, the present day volume of carbonates was already in existence during the Archean and contained Archean Sr isotopic ratios. Taking the recycled carbonate Sr to be most of the total Sr recycled through the oceans, this might account for the deviation between the calculated crustal and measured sea water curves, which is about one half of the difference between the crustal and Archean values. For the reasons discussed in Chapter 9, however, I do not believe that the recycled carbonate Sr formed the majority of marine strontium and thus this explanation would not be a satisfactory solution.

(c) There is a certain amount of recycling of crustal material (or radiogenic Sr) through the mantle as suggested by Armstrong (1968) and to some extent by Armstrong (1971b), Jakes and White (1971) and others. Assuming a complete fractionation of the continental crust at about 3.0 b.y. ago and its recycling through the mantle by 12% of the total crust/300 m.y. ($3\ km^3\ year^{-1}$), the model evolution should be as indicated in figure 48.

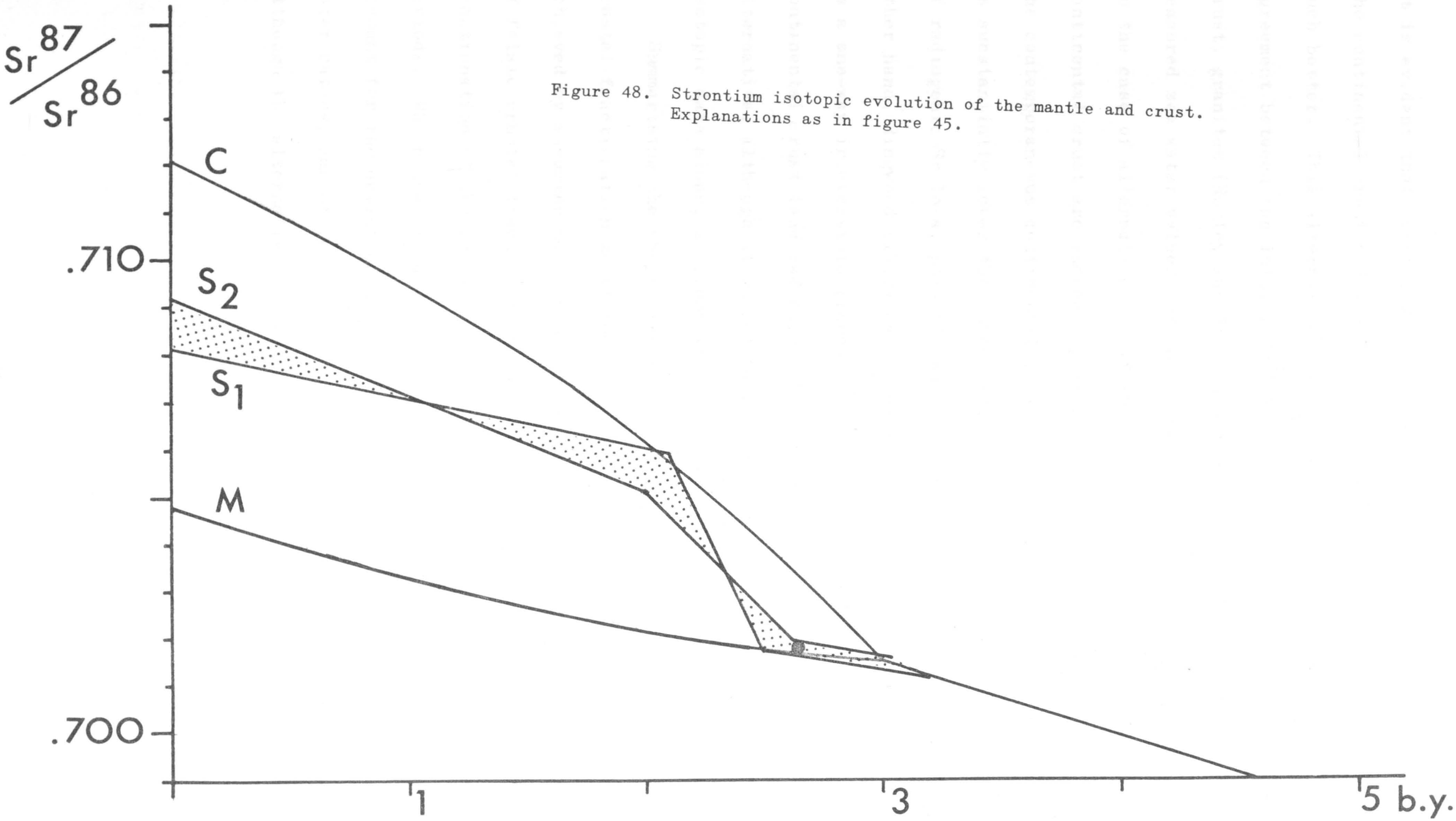


Figure 48. Strontium isotopic evolution of the mantle and crust. Explanations as in figure 45.

It is evident that recycling would lead to lower Sr isotopic values for the continental crust and the fit between such crust and sea water is much better. This alternative might be supported by an excellent agreement between the initial Sr^{87}/Sr^{86} ratios of the upper continental crust, granites (Hurley and Rand, 1969; Gerling et al., 1968) and measured sea water values for the Phanerozoic and Proterozoic, particularly in the case of alternative 2. If the $(Sr^{87}/Sr^{86})_0$ of granites and upper continental crust are indeed representative of the average Sr^{87}/Sr^{86} of the contemporaneous continental crust, the radiogenic Sr^{87} of such crust is substantially lower than predicted. This might indicate some degree of radiogenic Sr loss, possibly through exchange with the mantle. On the other hand, Ringwood (1969) maintains that the fractionation of the crust is a one-way irreversible process and there is no resorption of the continental crust (and radiogenic Sr?) into the mantle. Thus this alternative, although it cannot be rejected on the basis of strontium isotopic data alone, is probably not a very good solution to the problem.

Summarising the above discussion, the best fit between a simple crustal fractionation model and the sea water Sr isotopic curve is achieved by assuming mafic continental crust in Archean, a strong phase of felsic crustal fractionation in the Late Archean and continuous fractionation of the felsic crust at a lower rate during younger geological periods. Which one, if any, of the three listed alternatives might best account for the deviation between the calculated crustal and measured sea water ratios, cannot be ascertained on the basis of the present data, although the alternative (a) is favoured.

Chapter 11

CARBONATES AND CARBONATITES

The problem of possible metamorphic alteration of elemental Sr and its isotopes was not discussed in any detail in the previous chapters. The origin of carbonatites and intrusive limestone bodies of uncertain origin is closely related to this problem.

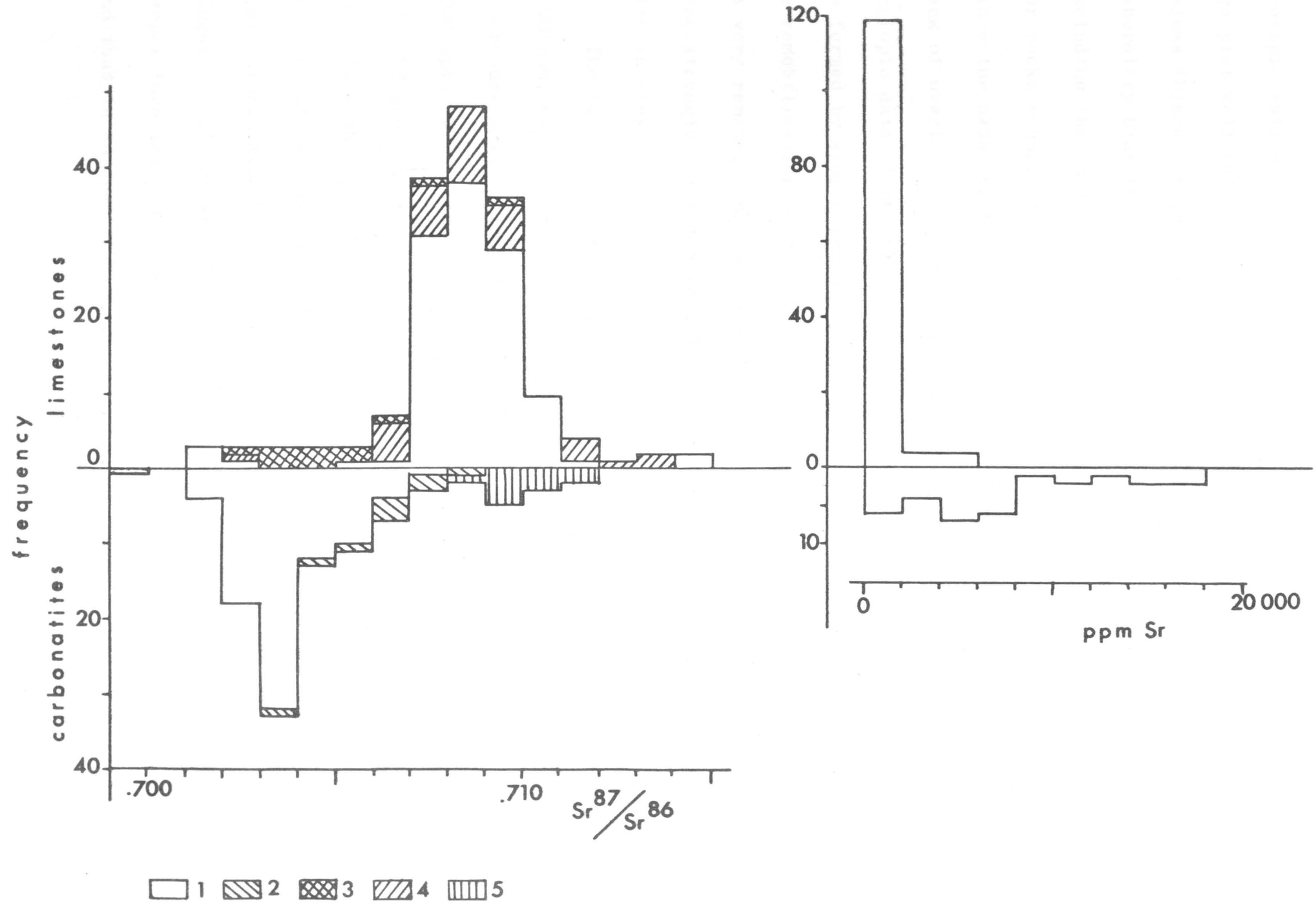
During the discussion of elemental Sr, it was argued that diagenesis and/or metamorphism would lower its concentration in carbonates. This feature was clearly demonstrated in fig. 35. Although there is some exchange of Sr between silicate and carbonate phases during deep burial anadiagenesis and epidiagenesis, this feature is probably restricted to a very small scale (see Chapter 10). Thus in relatively pure carbonate rocks the Sr isotopic contamination should remain negligible. Similar behaviour might be expected even during dry metamorphism. Comparison of Sr^{87}/Sr^{86} of the metamorphosed and unaffected Cambrian Ottertail Limestones of British Columbia (Deans et al., 1966) confirm this conclusion beyond any reasonable doubt. The preservation of probable original Sr isotopic ratios in the completely recrystallized Trenton Limestone xenolith (18 x 24 inches) surrounded by the Mont Royal Gabbro intrusion (Powell, 1966) would indicate that this ratio is not easily altered even under extreme temperature conditions. This leads to the conclusion that a significant alteration could only occur with "wet" metamorphism and/or metasomatism. Gittins et al. (1969) published Sr isotopic values from 0.709 for less altered Grenville Marbles, to 0.7021 for calcite-alkali feldspar-biotite hybrid rock formed between granite pegmatite and Grenville Marble. According to their explanation this may be caused: (a) "by Sr^{87}/Sr^{86} ratios of limestones covering the complete range of basalts, carbonatites and

limestones", or (b) "that limestones do not preserve their initial ratio throughout extensive metamorphism but undergo considerable adjustment, either by isotopic fractionation or by introduction of Sr with a different value of Sr^{87}/Sr^{86}".

The Grenville Province is unfortunate for this type of study, because only the upper boundary is known with any accuracy (Grenville Orogeny, ~1000 m.y.). The lower boundary is very uncertain and for example Krogh et al. (1969) reported muscovite Rb-Sr ages as high as 2.5 b.y. from the Grenville front in the Chibougamau-Surprise Lake area. Although such old ages are probably atypical, ages as young as 2.0 b.y. could account for original variations in Sr isotopic ratio between 0.705 and 0.709. The introduction of Sr with different Sr isotopic values is a more likely process responsible for the decrease in Sr^{87}/Sr^{86} ratio. The strong positive correlation between the amount of pegmatitic minerals and nonradiogenic Sr in the Grenville samples clearly indicates an external magmatic origin for the nonradiogenic Sr.

This brings us to the problem of carbonates and carbonatites. Carbonatites as opposed to sedimentary limestones have very low Sr^{87}/Sr^{86} ratios and very high Sr concentrations (fig. 49). The carbonatite part of this figure is a compilation from the literature (Powell, 1966, 1965a,b; Deans et al., 1966; Gittins et al., 1969; Bell and Powell, 1969, 1970; Powell et al., 1962; Hamilton and Deans, 1963; Deans and Powell, 1968; Powell and Hurley, 1963; von Eckermann, 1966; Quon and Heinrich, 1966 and Mendes and Canilho, 1968). The limestone part is based on data from the present thesis, and the analyses listed in Brookins et al. (1969), Powell (1966) and Gittins et al. (1969). Although there is some overlap in Sr isotopic values, the data show a clear boundary at 0.707. This supports the view of Powell and Hurley (1963) and Hamilton and Deans (1963) that

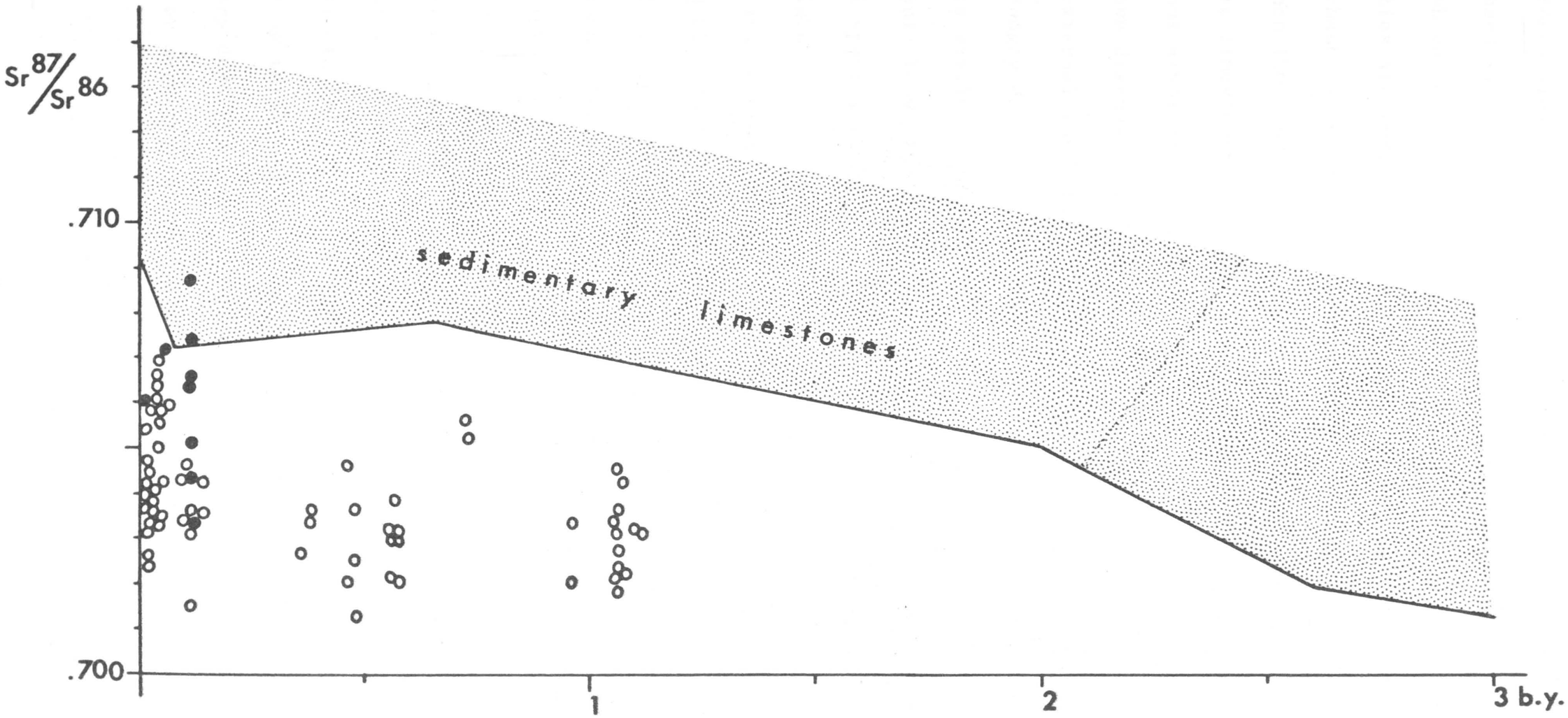
Figure 49. Histograms of Sr and Sr isotopic ratios in sedimentary limestones and carbonatites.
Explanations:
(1) Present data and references listed on p. 133.
(2) Hamilton and Deans (1963)
(3) Gittins et al. (1969)
(4) Powell (1966)
(5) Mkwisi, Keshya and Cape Verde Islands "carbonatites".


frequency
limestones
carbonatites
40
20
0
20
40
.700
.710
Sr^{87}/Sr^{86}
1
2
3
4
5
120
80
40
0
10
0
20 000
ppm Sr

in general the Sr isotopic values might be used for the recognition of carbonates and carbonatites, or at least for recognition of Sr from the two alternative sources. There is however some chance of similar Sr isotopic ratios. As seen from fig. 50 almost all carbonatites with known age plot well below the possible lower limit for limestones. The higher values (black circles) of Hamilton and Deans are anomalous and may represent laboratory bias (Eimer and Amend standard measurement not published). Excluding the analyses of Hamilton and Deans, it seems quite clear that for rocks younger than 1 b.y. the 0.707 value is a satisfactory boundary. Since the older carbonatites are <0.706 this would possibly indicate a lack of overlap for rocks as old as 1.5 b.y. Thus on the basis of Sr isotopic data alone, it seems unlikely that apparent carbonatites could be formed by simple remobilization of carbonates. The only exception could be remobilization of the old carbonate rocks (>2 b.y.). Such a possibility is very remote, since carbonate rocks of similar age are quite rare and are also strongly dolomitic or only dolomites. It is an unlikely possibility also in view of Sr abundances.

The concentration of elementary Sr in carbonatites is between 1000 and 20000 ppm, with the mode about 4000 ppm (fig. 49). From a review of the literature only two samples of Alnö carbonatites had a Sr content below 1000 ppm. The limestones on the other hand have average Sr content of only 452 ppm and values above 1000 ppm are rare (10% in the present thesis). The values above 2000 ppm are typical only for metastable aragonites. No measurements of the partition coefficient between liquid and calcite at temperatures typical for carbonatite magmas (about 600°C, Wyllie and Biggar, 1966) are known to the present author. Extrapolating from low temperature data (Oxburgh et al., 1959) the coefficient would be ≤ 0.07 and thus in an open system the liquid in equilibrium with carbonatitic

Figure 50. Plot of Sr^{87}/Sr^{86} of carbonatites and sedimentary carbonates vs. geological age.
Explanations: The full circles (measurements of Hamilton and Deans, 1963) are suspected to be too high.


Sr^{87}/Sr^{86}
.710
.700
sedimentary limestones
1
2
3 b.y.

calcites should have $(^{m}Sr/^{m}Ca)_{L}$ at least 1.6×10^{-2}, which is above any reasonable concentrations of Sr in sedimentary calcites. Assuming a complete closed system of melting of carbonates, the change of carbonatites having Sr concentrations 1000-2000 ppm is about 10%. The required Sr isotopic ratios are very low and satisfied only by very old carbonates, and so the chance is even lower, because their Sr content is generally much less than 1000 ppm. Older carbonates are also in general dolomites and dolomitic limestones and their closed system melting would produce MgO concentrations atypical for carbonatites.

The above discussion indicates that Sr in practically all carbonatites must be of external (probably magmatic) origin. The calculations for other elements strongly enriched in carbonatites (Ba, P, Th, U, Re etc.) would probably give similar results.

This would leave three possible modes of carbonatite origin:

(a) all species (CaO, Sr, volatiles etc.) are of magmatic (mantle?) origin

(b) Sr and possibly part of volatiles are of magmatic, whereas CaO and CO_2 are of sedimentary origin

(c) all species are of sedimentary origin and all observed carbonatites represent residual melts strongly enriched in Sr (and other elements) vs. $CaCO_3$ by some process of crystal fractionation.

The last alternative is unrealistic because complementary Sr-poor igneous accumulative carbonates are not observed and their dilution into melts of silicate (?) type is unlikely due to their limited miscibility.

Concluding this discussion, one might postulate that Sr isotopic and elementary data should be sufficient to discriminate between its sedimentary or magmatic origin. The data cannot discriminate between the

two alternative sources of $CaO(CO_2)$, although the first alternative is strongly favoured, not only by Sr and its isotopes, but also by experimental as well as field data (see the references at the beginning of this chapter).

The high Sr^{87}/Sr^{86} values (0.708-0.712) and low Sr concentrations for the Zambian Keshya and Mkwisi "intrusive limestones" might be consistent with remobilization of an original sedimentary limestone and/or sialic contamination. This problem was widely discussed in the literature and is beyond the scope of this thesis. The data for Cape Verde Islands "carbonatites" (Mendes and Canilho, 1968) are probably erroneous, since according to Allègre et al. (1971) the rocks contain typical Sr^{87}/Sr^{86} (0.703) and Sr (13000ppm) values.

For the reasons stated previously the Grenville Marbles and possibly also the carbonate vein-dikes of Powell (1965c) might be regarded as examples of the type (b) origin.

Chapter 12

A MODEL OF THE EVOLUTION OF SEDIMENTARY ROCKS

The discussion of this subject is very speculative and it is very difficult to take into account all relevant data. Therefore the discussed model may be only a crude approximation to the natural situation and, in many cases, the interpretation may be equivocal.

It is clear from published data (Ronov, 1964, 1968, 1971; Cloud, 1969, 1971; Engel, 1963; Rutten, 1962, 1966 and others), together with the data accumulated in this thesis (Chapter 2) that the compositions and relative abundances of different types of sedimentary rocks have varied with time. The evolutionary changes are indicated also by chemical trends summarised by Ronov and Migdisov (1970, 1971) and supported by the present data (Chapters 10 and 8).

The major changes observed are:

(1) Predominance of graywackes in Archean sequences, high proportion of arkoses in Early Proterozoic rocks, and a subordinate role of these immature sediments in younger periods, which are characterised by mature monomineralic sandstones, shales and carbonates;

(2) Widespread development of banded iron ore formation in sequences 3400-1800 m.y. old and their virtual absence in younger periods;

(3) Appearance of red beds at about 2000-1800 m.y. ago and their frequent occurrence in sequences younger than 1000 m.y.;

(4) Very rare Ca-Mg carbonates in the Archean and their ubiquity in younger periods. The carbonate rocks underwent probably the most distinctive evolutionary changes. Except for siderite, which was part of the banded iron ore formations, the oldest sedimentary carbonates were predominantly ferrugineous, early diagenetic (and primary?) dolomites.

Their Fe content decreased with time. These dolomites were abundant in sequences 2500-600 m.y. old. Inorganic and biochemical limestones started to dominate at about 1000 m.y. ago. Since approximately 600 m.y. ago the predominant carbonate rocks were neritic organic limestones, which were replaced by pelagic limestones at 150 m.y. ago;

(5) Common presence of sedimentary phosphates since Middle Riphean and Middle Sinian (Bushinskii, 1966). The stratigraphy of the oldest known phosphate deposits is very uncertain, but they are very likely not older than about 1000 m.y. Phosphates, however, have been abundant mainly since the uppermost Proterozoic and Cambrian;

(6) Presence of sedimentary Ca-sulphates in rocks younger than 600 m.y. Ca-sulphates in Precambrian sequences are very rare and known only from few localities. The age of the oldest occurrence (Grenville Province) (Engel, 1963) is uncertain, but is unlikely to be older than about 1.5 b.y. The second occurrence (Bitter Springs Formation of Central Australia, p. 22) is very likely a maximum of 1.0 b.y. old. The other occurrences are close to the Cambrian boundary;

(7) Presence of salts in formations younger than 600 m.y. However, pseudomorphs after NaCl are known throughout the whole Proterozoic sequence;

(8) Coal formations since approximately 350 m.y. ago.

The above listed changes are probably not exhaustive and do not represent a comprehensive treatment of the subject. They are however sufficient to illustrate the evolution of sedimentation. The ages given are not very rigorous boundaries, and they also do not mean that some rocks did not appear at all before or after the periods listed. They only serve to delineate the periods in which particular rock types were most dominant.

The evolution of sedimentary rocks was accompanied by simultaneous evolution of organic life, which started before 3200 m.y. ago (Engel et al., 1968). Organic evolution was marked by the appearance of the first animals at about (1000?)-800 m.y. ago (Glaessner, 1968) and by the later explosion in the Cambrian, and migration on continents in the Silurian-Devonian.

The predominance of graywackes in Archean and arkoses in the Early Proterozoic could be explained by changes in the composition of the source regions (upper continental crust). A predominantly mafic crust during the Archean could account for graywackes, whereas the granitic bodies, which were formed during the phase of strong felsic fractionation in the Late Archean, served as the source for arkoses during Early Proterozoic. The problem of crustal evolution has been discussed in detail in Chapters 8 and 10.

With development of a sedimentary cover and continuous recycling of sediments, the immature rocks were reworked into more mature sandstones, shales and carbonates, and certain elements (predominantly Na) released into sea water.

This simple explanation would not however account for the evolutionary changes indicated by inorganic, biochemical and organic deposits. Their summary is given in Table 10.

Table 10

Open shelf and pelagic environments	Semi-barred environments	Terrestrial environments
pelagic biogenic limestones (150 m.y.-present)		coal formations (350 m.y.-present)
biogenic neritic limestones (600 m.y.-present), phosphatic(?) in early stages	salts (600 m.y.-present)	
	Ca-sulphates (600 m.y.-present)	
inorganic and/or biochemical limestones (1000 m.y.-present)		
Ca-phosphates (1000 m.y.-present)		
		red beds (1800 m.y.-present)
	early diagenetic dolomites (2500-600 m.y.)	
banded iron ore formations (3300-1800 m.y.)		

The environmental classification is only a generalization, and there was certainly an overlap for various facies. However accepting these limitations, the scheme may be used with confidence for the discussion below.

The question is whether this apparent evolution was a primary feature or reflects only postdepositional changes.

Garrels and MacKenzie (1969, 1971a, Chapter 10) calculated that the entire mass of sediments deposited during the history of the earth was about five times their present load. Due to differential solubility and recycling, the least soluble rocks were recycled and destroyed less rapidly and thus "appeared" earlier in the stratigraphic record. The calculated "half mass ages" were 600 m.y. for shales and sandstones, 300 m.y. for carbonates and

200 m.y. for evaporites. This factor is certainly very important and a substantial degree of the observed changes, particularly the relative proportion of different rock types, could be ascribed to this phenomenon. Nevertheless, several observations are difficult to explain by this factor.

The presence of banded iron ore formations in the interval 3300-1800 m.y. is beyond any reasonable doubt a primary feature. If so, the increasing Mn, Fe concentrations with age were very likely primary features of carbonate rocks as well. The solubility of Mn species is somewhat higher than the solubility of Fe compounds. Consequently postdepositional changes should lower the Mn/Fe ratio in carbonate rocks. However, the observed trend is just the opposite and this is a further indication that the observed trends were original features of the rocks. It is maintained (p. 76) that the most likely factors causing this evolution were changes in P_{CO_2} and P_{O_2} of the atmosphere. This interpretation might be valid regardless of what proportion of the Fe^{2+}/Fe^{3+} trend was caused by diagenesis and/or metamorphism.

Similarly the presence of cherts and chert layers in banded iron ore formations indicates that the increasing content of chalcedony in carbonate rocks with age was also a primary feature.

The increasing dolomite/limestone ratio with age theoretically could be interpreted as a postdepositional phenomenon. The Proterozoic dolomites were, however, quite clearly of early diagenetic (and primary?) origin (see Chapter 2) and thus the required dolomitization must have been during a very early stage. This again supports my interpretation of the Mg/Ca trend as a primary feature, caused probably in its major part by a higher P_{CO_2}.

The solubility product of apatite is $\sim 10^{-60}$ (Krauskopf, 1967, appendix 7), yet sedimentary phosphates in economic quantities were deposited only since Middle Riphean and Sinian ($\sim$1000 m.y.?) and mainly since Cambrian time (Cloud, 1971; P.J. Cook, personal communication, 1971; Bushinskii, 1966),

whereas for example limestones, dolomites and siderite are known from much older sequences.

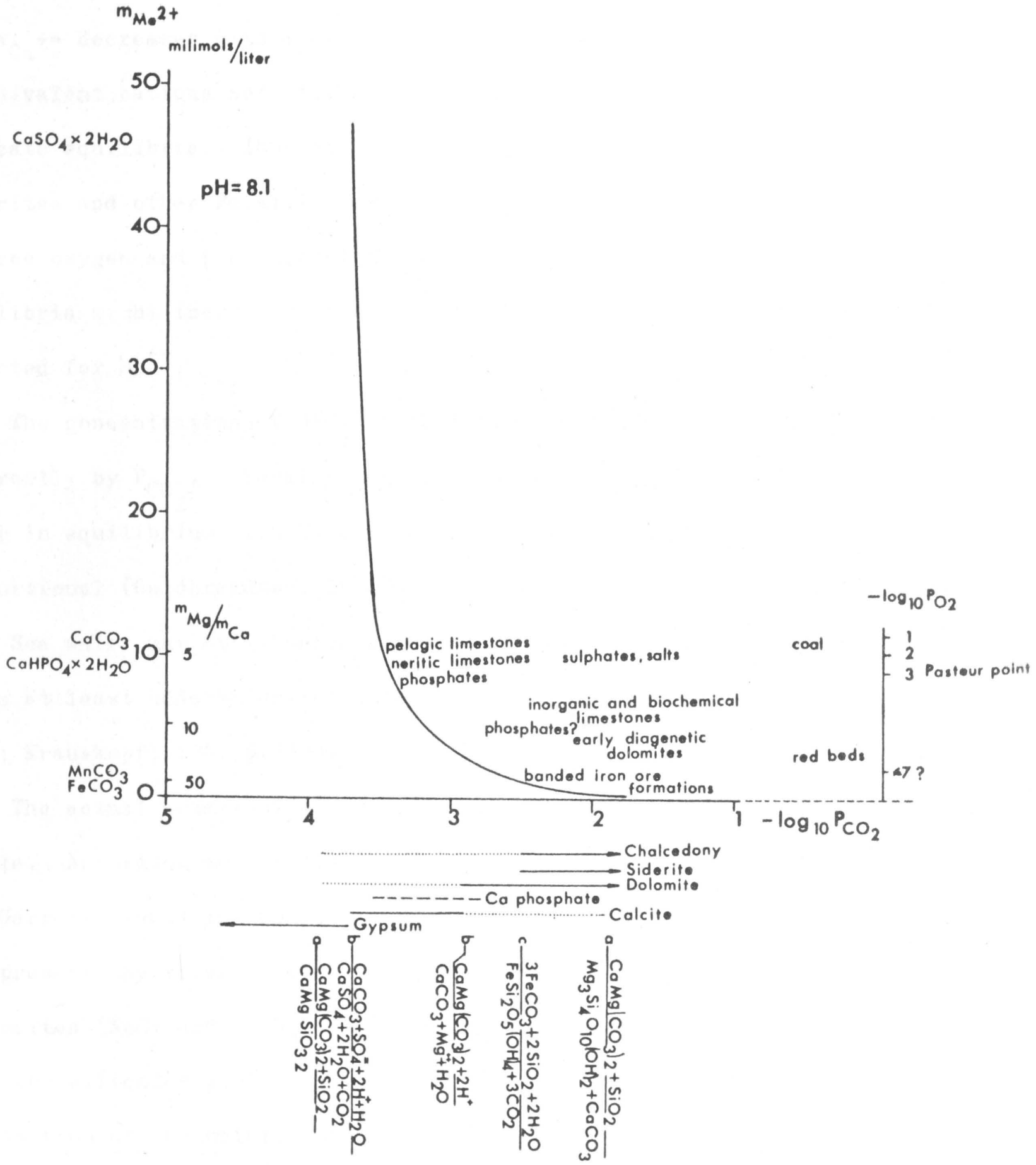
The above listed arguments indicating that the trends summarised in the table might be in part original features would demand an alternative explanation based on more than the recycling of sediments. During the discussion of possible limits on the composition of the crust, atmosphere and hydrosphere (Chapter 8) it was concluded that the two most likely variables were P_{O_2} and P_{CO_2}. The probable changes of P_{CO_2} were about one order of magnitude with its present value close to the lower limit, regardless of the nature of ocean buffering. The upper limit of P_{O_2} was accepted as being close to its present value, whereas it was not possible to set up the lower limit with any confidence, except as "nonequilibrium quantities". For the present purposes it will be assumed that the lower limit was close to the value in volcanic gases in equilibrium with Fe^{2+}/Fe^{3+} of basaltic melts.

With those assumptions ($P_{CO_2} \sim 10^{-2.5}$ and $P_{O_2} \sim 10^{-7}$), I have constructed the model presented in fig. 51. The period discussed will be only from the Archean (3 b.y.) onward and the older stage will not be considered, since the preserved record is very poor.

Since the publication of Sillén's (1961) paper it has become generally accepted that the ocean is an approximate "equilibrium product" of excess volatiles and silicates and thus its chemistry, with respect to its major species, is relatively stable (see the references on p. 66). The early stages of the earth's history might be an exception to this pattern.

The buffering properties of aluminosilicates are pH dependent, but at the pH typical for sea water the buffer intensity of kaolinite alone is approximately 10^3 higher than the buffer intensity of carbonates (Stumm and Morgan, 1970, p. 419). This would indicate that the pH of the ocean is a very conservative property and is maintained by silicates, although the short

Figure 51. Diagrammatic presentation of the evolution of sedimentary rocks in geologic history.
Explanations: The saturations with respect to species marked on the y-axis are for present day conditions only.
(a) Holland (1965)
(b) Stumm and Morgan (1970)
(c) Garrels and MacKenzie (1971a).


$m_{Me^{2+}}$
milimols/liter
50
40
30
20
10
0
$CaSO_4 \times 2H_2O$
pH = 8.1
m_{Mg}/m_{Ca}
$CaCO_3$
$CaHPO_4 \times 2H_2O$
5
10
50
$MnCO_3$
$FeCO_3$
pelagic limestones
neritic limestones
phosphates
sulphates, salts
coal
inorganic and biochemical limestones
phosphates?
early diagenetic dolomites
red beds
banded iron ore formations
$-\log_{10} P_{O_2}$
1
2
3 Pasteur point
47 ?
5
4
3
2
1
$-\log_{10} P_{CO_2}$
Chalcedony
Siderite
Dolomite
Ca phosphate
Calcite
Gypsum
a $CaMg(CO_3)_2 + SiO_2 \rightarrow Mg_3Si_4O_{10}(OH)_2 + CaCO_3$
c $3FeCO_3 + 2SiO_2 + 2H_2O \rightarrow Fe_3Si_2O_5(OH)_4 + 3CO_2$
b $CaMg(CO_3)_2 + 2H^+ \rightarrow CaCO_3 + Mg^{++} + H_2O$
b $CaCO_3 + SO_4^{--} + 2H^+ + H_2O \rightarrow CaSO_4 + 2H_2O + CO_2$
a $CaMg(CO_3)_2 + SiO_2 \rightarrow CaMgSiO_3 + 2CO_2$

term control is exercised by carbonates (see the references on p. 68). Holland (1965) claimed that in a silicate-buffered ocean activities of a_{K^+}/a_{H^+}, a_{Na^+}/a_{H^+} and $a_{Mg^{++}}/a_{H^+}$ are fixed by equilibria with clay minerals, whereas Ca is largely controlled by carbonate equilibria. Thus at fixed pH the $a_{Ca^{++}}$ decreases with increasing P_{CO_2}. This would apparently be true for any divalent cations not utilised, or only partly utilised, in the above silicate equilibria. Thus Fe^{++} might be partly fixed by equilibria with chlorites and other Fe silicates and possibly with magnetite. In the absence of free oxygen and presence of higher HCO_3^-, the role of siderite in Fe^{++} equilibria might increase quite considerably. Similar behaviour might also be expected for Mn^{++}.

The concentration of $HPO_4^=$ in solution is maintained by $a_{Ca^{++}}$ and thus indirectly by P_{CO_2}. Therefore the concentrations of $HPO_4^=$ and HCO_3^- in sea water in equilibrium with Ca-carbonates and Ca-phosphates are directly proportional (Guldbrandsen, 1969).

Sea water may still serve as an accumulation reservoir for Cl^- and $SO_4^=$, or is at least undersaturated with respect to gypsum and halite (Holland, 1965; Krauskopf, 1967 p. 323).

The actual behaviour of any particular ion in sea water is not that simple. According to Garrels and MacKenzie (1971, p. 283) and MacKenzie and Garrels (1966) the composition of sedimentary rocks which might balance the present day river discharge would be represented by about 28% of evaporites (NaCl and $CaSO_4$), 26% of carbonates and 41% of clay minerals. Thus the silicates would not be the only controlling factor of the ionic composition of sea water. However, disregarding this argument, Holland's conclusions may be accepted as an indicator of the direction in which the ionic ratios in sea water would be altered by variables such as CO_2 and O_2.

In the Archean the abundant mafic and intermediate volcanics and graywackes were attacked, giving rise to large amounts of divalent cations and H_4SiO_4 (decomposition of plagioclase and other silicates). Due to the low P_{O_2} and higher P_{CO_2} in the contemporaneous atmosphere, the divalent Fe and Mn would not be oxidized and could be transported into the oceans as bicarbonates. The mineral-ocean interactions at this stage are presented by Garrels and MacKenzie (1971a, p. 294) as:

(a) $14\ H_2O + 6\ NaAlSi_3O_8 + 3\ FeCO_3 + 15\ MgSiO_3 + CaCl_2 =$

$= 22\ SiO_2 + 6\ NaCl + 3\ Mg_5Al_2Si_3O_{10}(OH)_8 + 3\ CaCO_3 + Fe_3Si_2O_5(OH)_4$

(b) $5\ MgSiO_3 + CaAl_2Si_2O_8 + CO_2 = Mg_5Al_2Si_3O_{10}(OH)_8 + CaCO_3 + 4\ SiO_2$

(c) $Fe_3Si_2O_5(OH)_4 + 3\ CO_2 = 3\ FeCO_3 + 2\ SiO_2 + 2\ H_2O$

According to Krauskopf (1967, p. 82) the possible concentrations of Fe^{++} and Mn^{++} in equilibrium with the present day HCO_3^- of sea water would be 0.08 and 0.15 milimols/liter respectively. This alone would be sufficient to stabilize siderite against calcite ($^mCa^{++}/^mFe^{++} < 150$). If the activity of Ca^{++} is controlled largely by carbonate equilibria and that of Fe^{++} only partly so, the greater decrease in $a_{Ca^{++}}$ could result in even lower $^mCa^{++}/^mFe^{++}$ ratios. The above discussion might indicate that $CaCO_3$ might have been precipitated only under limited conditions, with small concentrations of divalent iron. Its precipitation might have been aided by biochemical processes of blue-green algae. On the other hand, the precipitation of Fe and Mn carbonates (together with their silicates, pyrite and magnetite) and cherts could have been achieved even within open shelf conditions. This explanation might account for the lack of detrital material, the undisturbed nature of banding and the wide lateral spread of the banded iron ore formations. It is interesting to note that Strakhov (in Ronov, 1964) advocated even a pelagic sedimentary environment for these rocks.

This explanation might also account for the high proportion of $(Fe,Mn)CO_3$ and low proportion of limestones and consequently of dolomites in the Archean sequences. Formation of dolomites probably requires a $CaCO_3$ precursor and thus lack of $CaCO_3$ precursors might be the cause of the low proportion of dolomites.

On the other hand such an interpretation creates some difficulties in understanding the Ca^{++} cycle. Apparently Archean weathering would have also liberated substantial quantities of Ca^{++}. Since it was postulated that Ca^{++} concentration in sea water would be maintained by equilibria with $CaCO_3$, one would expect voluminous limestones and dolomites in Archean sequences (unless there was a strong subtraction of Ca^{++} with iron ores or other species). Since this does not seem to be the case, preferential leaching of limestones and dolomites, relative to the banded iron ore formations, might be the cause of their low abundance in the Archean.

Higher P_{O_2} and lower P_{CO_2} at about 2.5 b.y. ago could lead to an increase in the Ca/Fe ratio (by oxidation of the part of divalent Fe and Mn and possibly also due to silicate equilibria) and to a decrease in the Mg/Ca ratio of sea water. The higher Ca/Fe ratio might stabilize $CaCO_3$ against $FeCO_3$ in broader sedimentary environments. The $^{m}Mg/^{m}Ca$ ratios of sea water at this period (~ 50) are close to the values observed in present day environments with early diagenetic dolomite formation (cf. Friedman and Sanders, 1967). Evaporation in semi-barred basins and biochemical reactions (blue-green algae and bacteria) could increase the $a_{Ca^{++}}$ to the degree of saturation with respect to $CaCO_3$ much more easily than during earlier periods. The precipitated phase at this Mg/Ca ratio would very likely be aragonite (cf. Müller et al., 1971), which would be very quickly altered during early diagenesis into dolomite by sea water with a high Mg/Ca ratio. This could account for the almost completely dolomitic nature of carbonate sequences

older than about 1000 m.y. ago, as well as for their littoral and semi-barred facial association.

At about 1800 m.y. ago the atmospheric P_{O_2} was such that Fe^{++} and Mn^{++} in continental sediments and waters were oxidized and remained disseminated in residual terrestrial sediments. This might account for the disappearance of banded iron formations and appearance of red beds. It is difficult to set a limit on P_{O_2} at this stage, but the absence of red beds in older periods might indicate almost complete absence of free oxygen in the contemporaneous atmosphere.

As P_{CO_2} decreases, the Ca concentration in sea water will increase and consequently Mg/Ca ratio decrease. The appearance of voluminous limestones in sedimentary sequences of littoral and semi-barred sedimentary environments at about 1000 m.y. ago would indicate a $^{m}Mg/^{m}Ca$ ratio of about 10, which is close to the lower limit of recent early diagenetic dolomite environments. The P_{CO_2} for coexisting dolomite and calcite (figure 51) was calculated on the assumption that $^{m}Mg/^{m}Ca$ was about 20 (Holland, 1965; Stumm and Morgan, 1970). At this stage the originally precipitated carbonate minerals could be high-Mg calcites and aragonites ($^{m}Mg/^{m}Ca < 25$).

The appearance of voluminous phosphates at approximately the same time as limestones is an enigma. Increasing P_2O_5 in younger sequences is indicated also by higher P_2O_5 contents in young iron ores than in their Archean and Early Proterozoic counterparts (Lepp and Goldich, 1964).

A rise of $HPO_4^{=}$ concentrations in sea water could lead to precipitation of Ca-phosphates and could also avoid their dilution by simultaneous precipitation of limestones (Guldbrandsen, 1969). The rise of $HPO_4^{=}$ concentration (without complementary rise in HCO_3^{-}) is generally achieved by direct or indirect organic activity. Perhaps there might be a correlation between the appearance of the first animals (1000?)-800 m.y. ago (Glaessner,

1968) and the appearance of the economic phosphate deposits. On the other hand the phosphates seem to slightly precede the appearance of the first animals. This and their present day accumulation together with $CaCO_3$ sediments might favour the high Mg/Ca ratio of older ocean water as the principal reason of their absence in older sequences.

This discussion immediately opens the Pandora's box of the evolution of organic life and its causes. It is generally agreed that the early stages of life processes required a non-oxygenic atmosphere (Oparin, 1961; Fischer, 1965; McAlister, 1968 and many others). A non-oxygenic atmosphere was also required to stabilize Fe and Mn carbonates, silicates, sulphides and magnetite against haematite as discussed previously. However, the timing and rate of the oxygen accumulation during later stages is still an open question. The problem is too complex for the present discussion, but there have been several attempts to equate the evolution of organic life with changing P_{O_2}. As yet the best discussion is probably the paper of Berkner and Marshall (1964). On the basis of H_2O and CO_2 dissociation by UV radiation they postulated that the inorganic equilibrium P_{O_2} in the primitive atmosphere would be $\sim 10^{-3}$ of the present atmospheric level (PAL). This calculation was questioned by Brinkman (1969) and to some extent by van Valen (1971) and thus it is difficult to set any limit for the early stages. However, the important contribution made by Berkner and Marshall is their emphasis on the "Pasteur point", which is 10^{-2} of PAL. At this point the lethal UV radiation is absorbed by the O_3 layer (which is dependent on P_{O_2}) and a few cm of water and organisms change from fermentation to respiration, which represents a net gain of energy from 20 to 675 cal/gram-mol. They argued that this point was achieved at about 600 m.y. ago and was the cause of organic explosion in Cambrian. Others (Rutten, 1962, 1966; Glaessner, 1968) pointed out that majority of the organic phyla were present in the

Cambrian and their soft bodies were often present in the younger Proterozoic. Rutten maintained that the appearance of highly evolved erganisms in such short time required precursors and so the apparent explosion in the Cambrian would be associated with formation of hard skeletons only. Somewhat higher P_{O_2} and O_3 at about 600 m.y. might also be indicated by stromatolites of that age. Lethal UV radiation at the "Pasteur point" should penetrate a few cm of water. Stromatolitic carbonates very often indicate an intertidal origin and thus due to the lack of water layer they would require a more efficient atmospheric shielding, in spite of the surprisingly high tolerance of blue-green algae to UV radiation (Fischer, 1965; McAlister, 1968). In any case it seems likely that the "Pasteur point" might have been achieved somewhere between 1000 and 600 m.y. ago.

At about 600 m.y. ago the $a_{Ca}{}^{++}$ might have been close to its present value. The resulting low $^{m}Mg/^{m}Ca$ ratio of sea water ($\geqslant 5$) could enable the precipitation of low-Mg calcite (strongly phosphatic in early stages?), possibly by organic activity. The actual reason for the secretion of skeletons is not known and the topic would require a great deal of speculation. The lower solubility of low-Mg calcite might enable $CaCO_3$ deposition even in deeper neritic environments.

The appearance of the voluminous sulphates at the beginning of Paleozoic might be explained in several ways. Ronov (1964) maintained that the appearance of sulphates was related to the increase in P_{O_2} and subsequent oxidation of $S^{=}$ to $SO_4{}^{=}$. This is an unlikely explanation since $SO_4{}^{=}$ would be the stable species of sulphur even at very low P_{O_2} pressures (Holland, 1962). Judging from the Eh-pH and P_{O_2}-P_{CO_2}-P_{S_2} diagrams of Garrels and Christ (1965), $SO_4{}^{=}$ should be stable at P_{O_2} pressures sufficient to oxidize Fe^{++} to Fe^{+++}. Therefore, $SO_4{}^{=}$ should be a stable species of sea water at least since the disappearance of the banded iron ore formations.

Another possible explanation might be based on the recycling model of Garrels and MacKenzie (1971a). The high solubility of Ca-sulphates would be consistent with this explanation.

A third possible explanation would be consistent with the present model. It is clear from fig. 51 that at P_{CO_2} close to its present value ($10^{-3.5}$) small changes in P_{CO_2} could produce large increases in $a_{Ca}{}^{++}$. Consequently, saturation with respect to gypsum might have been reached relatively easily, compared with earlier periods of the earth's history. If this is true, it might indicate that the ocean still acts as an accumulatory system for $SO_4^{=}$, or more likely, that the $SO_4^{=}$ level in the ocean is maintained predominantly by oxidation-reduction phenomena (bacterial?) and not by the precipitation of evaporites.

The appearance of salts is probably best explained by recycling along the lines of the Garrels and MacKenzie model, since halite pseudomorphs are common in semi-barred sequences throughout the whole Proterozoic. If on the other hand this feature is accepted as a primary phenomenon, any explanation should be related to a continuous accumulation of Cl^- in sea water. The "corrected storage time" for Cl^- is only 230 m.y. and for Na^+ even less (108 m.y.) (Garrels and MacKenzie, 1971a, p. 109). Accepting the reasoning of Holland (1965), $a_{Na}{}^+$ in sea water should be approximately constant and thus the appearance of economic halite deposits could not be related to the increase in $a_{Na}{}^+$. However, if one excludes halite, there seems to be no other species (except for the possibility of buried concentrated brines), which could account for the subtraction of Cl^-. This difficulty seems to favour the explanation based on recycling.

At about 400 m.y. ago the P_{O_2} might have been close to 10^{-2} and this would provide enough shielding of continental environments from lethal UV radiation for plants and animals to appear on dry land in Silurian and

Devonian time (Berkner and Marshall, 1964), and consequently for the formation of coal deposits.

With the decrease in P_{CO_2} to the present value (150 m.y. ago), the low $^{m}Mg/^{m}Ca$ (= 5) of the surface layers of the warm open ocean allowed even pelagic organisms to secrete low-Mg calcitic skeletons, although inorganically this species would be stable only at $^{m}Mg/^{m}Ca$ ratios ≤ 1 (Müller et al., 1971). The existence of relatively stable low-Mg calcite skeletons made possible the formation of widespread deep sea sediments, which are dominant in the present ocean.

The P_{CO_2} quoted for the equilibria of different mineralogical parageneses are internal pressures of the parent solutions rather than atmospheric pressures. Nevertheless they would be at least proportional to the partial pressures in the contemporaneous atmospheres.

The above discussion is speculative and I do not wish to maintain that this is the correct explanation. The actual situation will be undoubtedly much more complicated than the picture outlined in this chapter. However, it is my belief that a combination of models along the lines suggested by Holland (1965), Berkner and Marshall (1964), Garrels and MacKenzie (1971a) and Ronov (1964) could lead to the development of a consistent model, which might help in further research into this problem. The model presented here is only a very crude attempt to explain the observed sedimentological evolution by as few variables as possible. Also the invoked changes in the variables are quite small, and the departure of this model from uniformitarianism is not very great. If this interpretation only stirs people more competent than myself to some elaboration, or even rejection, it will have served its purpose.

CONCLUSIONS

The interpretations in this thesis are consistent with the previously advanced hypotheses about the evolution of the earth's crust, hydrosphere and atmosphere. In particular, the Sr isotopic data and the variations in alkalies seem to support earlier suggestions about predominantly mafic composition of the continental crust in the Archean, a strong phase of felsic fractionation in the Late Archean and a continually more felsic nature of the continental crust during younger periods of the earth's history.

The evolution of the earth's atmosphere and hydrosphere was dominated by equilibrium reactions between excess volatiles and silicates and thus their composition was relatively stable. The two notable exceptions from this pattern were probably oxygen and carbon dioxide. The data on Fe, Mn, Ca and Mg seem to indicate very strongly that P_{O_2} increased and P_{CO_2} decreased during the course of geological history. Thus the above excess volatiles + silicate equilibria, although basically valid, were modified to some extent during the course of the P_{O_2} and P_{CO_2} evolution.

These two conclusions may be the most important contribution of the present thesis. The conclusions are not entirely original, but the data add additional support to the hypotheses based very often on different lines of evidence. Therefore I hope, that the thesis contributed at least marginally to the understanding of the evolution of the outer spheres of the Earth.

Appendix No. 1 - Chemical analyses

Sample	Dept. No. of sample	Total Fe as Fe_2O_3	MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	CO_2 (loss)	Σ	FeO	Fe_2O_3	Rb	Sr	Sr^{87}/Sr^{86}
		%														ppm		
Quaternary																		
1	70-819	0.063	-	0.007	50.825	0.140	0.059	3.688	0.195	0.036	n.d.	40.210	95.223*	0.032	0.027	0.51	3309	.70926
2	69-1224	0.254	0.013	0.041	33.410	0.361	0.057	25.072	0.519	1.513	n.d.	29.430	90.670*	0.146	0.092	4.35	5357	.70944
3	70-330	0.461	0.004	0.060	46.587	0.583	0.041	4.429	1.362	4.242	n.d.	41.411	99.180	0.102	0.343	17.56	382	.71684
Tertiary																		
4	69-1223	0.043	-	0.009	54.564	0.063	0.041	0.003	0.127	0.230	n.d.	43.060	98.140	0.014	0.027	0.12	4458	.70926
Cretaceous																		
5		0.351	0.025	0.061	48.908	0.179	0.192	6.732	1.888	1.346	n.d.	40.180	99.862	0.073	0.270	5.36	304	.70749
6		0.188	0.016	0.007	52.919	0.084	0.082	1.579	0.226	1.027	n.d.	43.150	99.278	0.053	0.129	1.64	301	.70731
7		0.188	0.026	0.007	52.211	0.118	0.123	1.849	0.284	1.676	n.d.	43.610	100.088	0.111	0.065	2.79	773	.70750
8		0.568	0.013	0.054	32.439	0.277	0.060	39.281	1.277	0.834	n.d.	25.589	100.392	0.260	0.279	11.11	344	.70732
9		1.928	0.101	0.175	43.310	0.800	0.084	16.468	4.109	2.135	n.d.	30.120	99.230	0.958	0.390	37.98	365	.70761
Jurassic																		
10		0.283	0.016	0.030	52.599	0.236	0.115	1.000	0.535	1.444	n.d.	43.430	99.688	0.113	0.157	6.01	165	.70798
11		0.116	0.005	-	53.849	0.235	0.106	0.499	0.283	1.031	n.d.	43.730	99.854	0.058	0.054	1.08	195	.70949
12		0.147	0.016	0.008	53.549	0.076	0.139	0.694	0.766	1.033	n.d.	43.730	100.158	0.085	0.053	2.29	184	.70826
13		0.989	0.105	0.101	39.560	0.516	0.099	23.937	2.136	0.426	n.d.	31.610	99.479	n.d.	n.d.	14.68	206	.70767
14		0.249	0.004	0.005	47.743	0.415	0.078	12.278	0.768	1.424	n.d.	38.070	101.034	0.101	0.137	9.74	120	.70796
15		0.094	0.005	-	53.818	0.076	0.049	0.250	0.139	1.885	n.d.	44.360	98.979	0.030	0.050	1.37	99	.70820
16		0.153	0.003	0.014	41.486	0.380	0.167	21.283	0.633	2.002	n.d.	34.510	100.631	0.057	0.090	10.24	112	.70784
Triassic																		
17		0.436	0.036	0.031	52.951	0.155	0.074	1.874	0.761	1.085	n.d.	42.690	100.093	n.d.	n.d.	4.71	504	.70802
18		0.764	0.016	0.064	51.323	0.339	0.092	2.890	1.359	1.071	n.d.	41.770	99.688	0.030	0.731	13.20	120	.70726
19		0.042	-	0.003	31.086	0.081	0.027	0.050	0.153	21.036	n.d.	47.600	100.078	0.018	0.022	0.63	46	.70767
20		1.706	0.058	0.143	26.512	1.025	0.029	11.550	4.107	15.307	n.d.	37.977	98.414	1.170	0.404	41.23	515	.70841
21		0.498	0.009	0.020	29.950	0.383	0.037	2.681	1.157	18.955	n.d.	44.653	98.343	0.356	0.103	10.31	141	.70803
22		0.815	0.019	0.070	27.173	0.918	0.054	6.567	2.129	19.109	n.d.	42.350	99.204	0.413	0.356	28.02	109	.70850
23		0.645	0.019	0.030	29.674	0.512	0.061	2.802	1.161	19.306	n.d.	45.120	99.330	0.441	0.155	11.85	119	.70891
24		0.074	0.005	-	54.436	0.025	0.049	0.121	0.515	0.962	n.d.	43.920	100.107	0.020	0.052	0.99	148	.70841
25		0.031	-	0.009	54.728	0.054	0.032	-	0.116	0.475	n.d.	43.820	99.265	n.d.	n.d.	0.01	133	.70815
26		0.377	0.019	0.034	32.317	0.435	0.051	2.855	1.144	17.916	n.d.	44.890	100.038	0.157	0.203	12.79	113	.70776
27		0.021	0.005	-	53.927	0.009	0.049	0.010	0.043	0.871	n.d.	44.080	99.015	0.013	0.007	0.03	171	.70751
28		0.063	-	-	53.839	0.050	0.033	0.370	0.206	1.396	n.d.	43.850	99.807	0.014	0.048	0.31	151	.70804
29		0.055	-	0.004	30.804	0.081	0.036	0.237	0.204	21.053	n.d.	47.290	99.764	n.d.	n.d.	0.56	53	.70798

Sample	Dept. No. of sample	Total Fe as Fe_2O_3	MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	CO_2 (loss)	Σ	FeO	Fe_2O_3	Rb	Sr	Sr^{87}/Sr^{86}
		%														ppm		
30		0.064	0.005	0.182	54.023	0.034	0.041	0.066	0.101	0.932	n.d.	43.660	99.108	0.010	0.053	0.43	114	.70836
31		0.030	0.004	-	48.962	0.026	0.050	0.031	0.063	5.471	n.d.	44.760	99.397	0.016	0.012	0.18	116	.70810
32		0.022	-	-	55.375	0.059	0.033	0.102	0.543	1.079	n.d.	43.140	100.353	0.013	0.008	0.01	148	.70869
33		0.032	-	-	54.626	0.025	0.033	0.121	0.120	1.096	n.d.	43.940	99.993	0.014	0.016	1.46	540	.70795
34		0.146	-	0.006	51.966	0.185	0.041	0.788	0.391	2.418	n.d.	44.020	99.961	0.098	0.037	4.13	1263	.70801
35		0.150	-	0.005	49.625	0.239	0.057	5.315	0.538	2.173	n.d.	42.160	100.262	0.056	0.088	4.83	425	.70772
36		0.204	0.003	0.013	47.082	0.228	0.042	1.066	0.492	7.128	n.d.	44.300	100.558	n.d.	n.d.	1.19	353	.70809
37		0.020	-	-	54.288	0.069	0.031	0.123	0.149	1.161	n.d.	43.870	99.711	n.d.	n.d.	0.19	135	.70816
38		0.032	-	-	54.626	0.042	0.033	0.083	0.561	0.880	n.d.	44.190	100.447	0.017	0.169	0.96	1328	.70832
39		0.084	-	-	53.494	0.084	0.033	0.333	0.235	1.025	n.d.	44.160	99.448	0.030	0.051	1.43	832	.70826
40		0.375	0.004	0.009	51.987	0.116	0.031	2.334	0.558	1.804	n.d.	42.750	99.968	n.d.	n.d.	2.07	1316	.70817
41		0.626	0.024	0.035	44.832	0.606	0.043	4.683	1.387	6.193	n.d.	42.060	100.489	0.192	0.413	14.24	195	.70828
Permian																		
42		0.084	0.005	0.030	53.148	0.109	0.074	0.398	0.148	0.900	n.d.	44.230	99.126	n.d.	n.d.	2.20	787	.70703
43		0.031	0.005	-	53.074	0.084	0.033	0.517	0.148	0.814	n.d.	44.460	99.166	n.d.	n.d.	2.90	886	.70733
44		0.045	-	-	53.944	0.018	0.043	1.262	0.046	0.833	n.d.	43.447	99.688	n.d.	n.d.	1.10	726	.70755
45		0.115	0.005	0.008	53.999	0.138	0.057	0.749	0.396	0.937	n.d.	43.400	99.804	n.d.	n.d.	2.70	922	.70781
46		0.262	0.037	-	54.435	0.026	0.033	0.252	0.140	1.103	n.d.	43.900	100.188	n.d.	n.d.	1.40	848	.70790
47		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	n.d.	n.d.	2.50	499	.70736
Carboniferous																		
48		0.053	-	-	53.722	0.009	0.025	0.056	0.052	1.013	n.d.	44.400	99.330	n.d.	n.d.	1.00	873	.70822
49		0.084	0.015	-	53.190	0.009	0.041	0.508	0.062	0.921	n.d.	44.400	99.230	n.d.	n.d.	3.20	892	.70799
50		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	n.d.	n.d.	2.60	638	.70804
51		0.074	0.026	0.008	54.008	0.034	0.041	0.455	0.130	1.059	n.d.	43.707	99.542	n.d.	n.d.	3.40	372	.70794
52		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	n.d.	n.d.	2.17	850	.70810
53	BMR 7/1	0.334	0.028	0.022	53.495	0.141	0.104	1.955	0.432	0.672	0.024	42.700	99.907	0.033	0.200	4.43	133	.70853
Devonian																		
54	BMR 449/I	0.119	0.008	0.011	54.229	0.132	0.063	0.779	0.346	0.789	0.034	43.520	100.030	0.037	0.078	3.52	226	.70855
55	BMR 448	0.306	0.039	0.023	53.935	0.226	0.137	1.172	0.618	0.730	0.028	43.130	100.344	0.054	0.159	6.03	167	.70891
56	BMR 456/6B	0.150	0.019	0.012	54.341	0.238	0.142	0.415	0.260	0.678	0.021	43.350	99.624	0.020	0.128	1.95	140	.70974
57	BMR 149/3A	0.159	0.008	0.033	53.360	0.331	0.144	2.023	0.659	0.677	0.025	42.580	99.999	0.057	0.096	7.30	139	.70916
58	BMR 459/75	0.414	0.028	0.022	52.730	0.207	0.080	2.266	0.506	0.788	0.030	42.390	99.461	0.026	0.264	4.65	220	.70844
59		0.861	0.043	0.098	41.163	0.535	0.053	14.964	2.382	2.996	0.403	35.740	99.238	0.544	0.256	23.50	1802	.70844
60		1.147	0.054	0.165	37.335	0.883	0.056	21.448	3.254	2.692	0.444	32.481	99.959	0.523	0.378	29.06	1499	n.d.
61		0.868	0.045	0.115	41.991	0.471	0.064	17.290	2.494	1.657	0.539	34.715	100.249	0.522	0.288	16.40	1413	n.d.
62		1.291	0.044	0.176	36.951	1.055	0.066	22.999	4.199	1.606	0.315	30.800	99.502	0.588	0.214	39.01	1866	.70873

Sample	Dept. No. of sample	Total Fe as Fe_2O_3	% MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	CO_2 (loss)	Σ	FeO	Fe_2O_3	ppm Rb	Sr	Sr^{87}/Sr^{86}
Silurian																		
63	70-803	1.892	0.074	0.229	36.571	1.015	0.074	21.519	4.232	1.692	0.394	30.750	98.442	1.107	0.662	40.86	534	.70993
64	70-804	0.534	0.036	-	53.878	0.096	0.041	0.387	0.357	1.050	0.015	43.490	99.884	0.301	0.200	0.01	989	.70887
65	70-805	0.417	0.046	0.031	51.210	0.249	0.067	3.341	0.676	1.326	0.040	41.800	99.203	0.221	0.171	5.21	898	.70869
66	70-806	0.272	0.026	0.020	51.647	0.309	0.075	3.964	0.638	1.231	0.023	41.700	99.887	0.134	0.123	6.77	357	.70883
67	70-807	0.168	0.037	0.021	52.262	0.249	0.050	3.432	0.541	1.139	0.010	42.190	100.099	0.092	0.066	4.81	279	.70922
68	70-808	0.084	0.047	0.008	52.274	0.139	0.041	2.234	0.376	0.856	0.008	43.570	99.637	0.046	0.033	3.96	138	.70926
69	70-802	0.875	0.138	0.105	45.788	0.322	0.052	11.274	2.178	1.196	0.568	37.450	99.946	0.344	0.493	11.27	174	.70962
Ordovician																		
70	70-830	0.792	0.004	0.107	46.318	0.635	0.052	8.070	2.354	1.735	0.168	38.291	98.526	0.304	0.250	23.69	930	.70836
71	70-831	0.270	0.004	0.019	51.741	0.215	0.050	2.252	0.726	1.794	0.067	42.540	99.678	0.111	0.147	5.01	781	.70803
72	70-832	0.549	0.004	0.062	48.446	0.541	0.068	4.755	1.524	2.409	0.047	40.810	99.215	0.204	0.180	16.22	749	.70837
73	70-827	0.392	0.004	0.039	47.602	0.354	0.043	5.442	0.972	3.544	0.077	41.190	99.659	0.206	0.163	8.53	356	.70803
74	70-828	0.331	0.004	0.040	49.175	0.319	0.043	4.687	0.903	2.581	0.088	41.580	99.751	0.147	0.085	8.20	374	.70989
75	70-829	0.357	0.004	0.028	48.104	0.277	0.059	4.733	0.769	3.706	0.068	41.390	99.414	0.161	0.089	6.19	366	.70832
76	70-833	0.206	0.005	0.020	52.160	0.212	0.049	2.692	0.545	1.605	0.040	42.420	99.954	0.075	0.123	3.37	378	.70864
77	70-834	0.219	0.005	0.020	52.883	0.241	0.058	2.658	0.735	0.981	0.035	42.740	100.575	0.083	0.127	3.32	390	.70898
78	70-835	0.237	0.005	0.021	53.541	0.203	0.057	1.697	0.572	0.655	0.042	42.800	99.830	0.085	0.143	4.21	540	.70839
79	70-836	1.090	0.037	0.043	53.550	0.249	0.025	2.209	0.756	0.112	0.013	42.090	100.174	0.145	0.618	6.56	206	.70916
80	70-825	1.660	0.054	0.196	34.295	1.229	0.085	26.438	4.557	1.466	0.206	28.510	98.696	0.766	0.394	45.60	246	.70969
81	70-826	1.731	0.054	0.185	34.697	1.208	0.093	26.102	4.425	1.487	0.200	28.840	99.022	0.945	0.681	43.85	255	.70992
Cambrian																		
82	70-346	0.471	0.046	0.031	52.046	0.403	0.041	4.244	0.606	0.309	0.061	41.140	99.398	0.107	0.222	6.38	268	.70994
83	70-347	0.406	0.046	0.109	48.288	1.206	0.069	8.986	1.721	0.366	0.036	38.110	99.343	0.207	0.176	20.18	289	.70961
84	70-348	1.130	0.054	0.102	42.536	1.175	0.061	9.486	1.940	4.500	0.043	38.160	99.187	0.679	0.375	21.04	138	.70914
85	70-344	0.321	0.056	0.043	52.076	0.468	0.051	5.288	0.759	0.258	0.046	40.605	99.971	0.154	0.150	9.14	174	.71015
86	70-345	0.428	0.036	0.043	50.518	0.713	0.042	5.159	1.252	0.572	0.048	40.460	99.271	0.223	0.180	12.76	211	.70998
87	70-349	0.878	0.045	0.083	45.465	0.821	0.061	8.008	1.549	3.753	0.322	39.030	100.015	0.348	0.491	14.26	146	.71046
88	70-350	0.447	0.046	0.052	47.622	0.625	0.061	10.024	0.992	1.408	0.039	38.730	100.046	0.157	0.156	9.84	109	.71033
89	70-351	0.322	0.049	0.033	51.654	0.422	0.088	4.058	0.666	0.818	0.021	41.410	99.541	0.177	0.125	6.54	158	.71033
90	70-342	0.369	0.128	0.023	30.202	0.354	0.027	2.468	0.627	20.032	0.043	45.670	99.943	0.211	0.135	5.73	71	.71053
91	70-343	0.618	0.045	0.116	43.121	1.169	0.062	13.484	2.206	2.683	0.091	36.300	99.895	0.469	0.097	25.88	169	.71022
92	70-845	0.237	0.027	0.020	48.796	0.241	0.219	8.128	0.540	0.994	0.021	39.790	99.013	0.101	0.125	4.81	293	.70924
93	70-846	0.329	0.007	0.019	46.930	0.110	0.083	8.480	0.472	2.888	0.027	40.170	99.515	0.061	0.169	3.36	281	.70998
94	70-843	0.186	0.012	0.005	31.172	0.035	0.044	0.165	0.110	20.450	0.039	47.220	99.438	0.093	0.083	0.77	28	.70986
95	70-844	0.293	0.021	0.052	22.686	0.100	0.053	23.911	0.680	15.933	0.048	35.440	99.217	0.053	0.234	1.97	23	.71039

Sample	Dept. No. of sample	Total Fe as Fe_2O_3	% MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	CO_2 (loss)	Σ	FeO	Fe_2O_3	ppm Rb	Sr	Sr^{87}/Sr^{86}
96	70-847	0.728	0.022	0.025	29.717	0.203	0.044	1.775	0.469	20.681	0.022	46.070	99.756	0.170	0.339	3.07	39	.71004
97	70-848	0.352	0.013	.0.014	30.479	0.063	0.056	1.527	0.252	20.719	0.046	46.700	100.221	0.143	0.193	1.29	37	.71015
98	70-850	0.086	0.007	0.009	49.560	0.140	0.080	0.808	0.187	4.920	0.031	44.110	100.238	0.040	0.041	1.62	59	.70940
99	70-851	0.328	0.027	0.007	48.826	0.108	0.120	1.103	0.197	5.195	0.023	44.150	100.084	0.053	0.269	1.50	70	.70929
100	69-1198	1.227	0.024	0.138	43.992	1.114	0.079	12.316	3.349	1.343	0.399	36.060	100.041	0.593	0.568	27.50	1171	.70899
101	69-1207	1.665	0.097	0.016	48.146	0.208	0.042	2.640	0.556	3.951	0.069	42.150	99.540	1.301	0.219	3.95	295	.70945
102	69-1208	0.897	0.024	0.031	51.947	0.383	0.041	2.803	0.708	1.030	0.034	42.100	99.998	0.196	0.679	5.65	276	.70980
103	69-1209	0.938	1.979	0.041	49.425	0.397	0.113	4.648	1.121	0.808	0.047	39.710	99.227	0.383	0.512	10.41	159	.71015
104	69-1210	0.852	0.056	0.098	49.295	0.747	0.093	7.144	2.133	0.165	0.033	39.000	99.616	0.126	0.712	26.11	153	.70940
105	69-1211	1.050	0.385	0.081	39.370	0.823	0.135	24.594	1.777	0.285	0.037	30.850	99.387	0.097	0.942	21.45	150	.71005
106	69-1212	1.281	0.190	0.060	41.437	0.754	0.194	20.211	1.585	0.485	0.086	32.780	99.083	0.413	0.822	19.42	222	.70965
107	69-1199	0.525	0.088	0.051	19.311	1.285	0.051	34.145	2.012	12.616	0.063	29.000	99.147	0.114	0.398	35.13	48	.71047
108	69-1200	1.372	0.188	0.102	27.078	0.379	0.064	9.517	1.651	18.350	0.056	41.120	99.877	0.056	1.310	12.33	63	.70956
109	69-1213	0.262	0.016	0.009	53.537	0.191	0.191	3.677	0.407	0.171	0.023	42.070	100.554	0.086	0.166	2.44	208	.70974
110	69-1214	0.210	0.026	0.021	53.801	0.207	0.215	3.711	0.368	0.010	0.025	41.770	100.364	0.039	0.167	3.11	107	.71017
Precambrian																		
Adelaide Geosyncline																		
111	69-1201	1.025	0.066	0.140	45.794	0.618	0.104	11.097	2.935	0.823	0.614	36.920	100.136	0.544	0.420	18.96	566	.70927
112	69-1202	1.372	0.188	0.102	27.078	0.379	0.064	9.517	1.651	18.350	0.420	41.120	100.241	0.650	0.650	12.33	63	.70956
113	69-1197	3.453	0.078	0.627	7.857	1.538	0.196	57.609	7.562	6.018	n.d.	12.918	97.856	1.289	2.013	51.76	79	.71297
114	69-1222	2.648	0.051	0.567	24.905	0.801	0.221	25.675	4.407	9.490	0.827	30.000	99.583	2.031	0.391	25.63	172	.70973
115	69-1203	1.669	0.046	0.410	45.952	0.419	0.146	10.795	2.184	1.078	0.296	37.620	100.615	0.674	0.920	11.85	570	.70747
116	69-1204	2.246	0.045	0.105	44.670	0.379	0.088	13.658	1.875	0.813	0.210	35.090	99.179	0.994	1.141	9.07	1215	.70742
117	69-1205	2.352	0.150	0.041	50.133	0.149	0.068	5.977	0.931	0.452	0.094	39.780	100.127	0.366	1.945	3.68	546	.70835
118	70-813	0.509	0.015	0.041	49.227	0.330	0.060	9.540	1.014	0.333	0.205	39.010	100.284	0.249	0.232	8.25	647	.70773
119	69-1206	0.750	0.024	0.096	48.012	0.509	0.066	10.473	1.642	0.697	0.327	37.430	100.026	0.480	0.282	13.36	625	.70762
120	69-1194	2.353	0.039	0.296	31.911	0.691	0.166	16.852	3.303	8.310	0.265	34.550	98.736	1.711	0.452	21.89	452	.70751
121	69-1195	0.921	0.025	0.051	48.248	0.191	0.217	4.899	0.815	2.928	0.053	41.240	99.588	0.547	0.313	4.96	532	.70746
122	69-1196	0.952	0.035	0.063	50.275	0.190	0.240	3.081	0.869	1.907	0.038	41.700	99.350	0.383	0.526	6.74	606	.70746
123	69-1219	5.474	0.039	0.909	5.845	2.679	0.259	59.011	11.076	4.492	n.d.	7.542	97.316	4.195	0.812	92.87	203	.70923
124	69-1220	4.687	0.040	0.890	8.989	2.292	0.246	58.314	9.634	3.065	n.d.	9.464	97.621	2.002	2.462	71.28	295	.70845
125	70-818	2.857	0.071	0.756	18.870	1.609	0.226	46.012	7.224	2.612	1.617	17.774	98.014	2.259	0.345	46.00	697	.70845
126	70-818	0.932	0.139	0.016	45.000	0.101	0.037	17.171	0.253	0.193	0.041	35.530	99.413	0.732	0.119	1.14	2015	.70869
127	70-812	6.297	0.188	0.862	4.773	2.678	0.207	54.916	12.155	6.223	n.d.	9.418	97.677	4.708	1.065	104.41	63	.71459
128	69-1193	5.705	0.108	0.891	7.531	2.383	0.224	55.104	11.345	4.561	n.d.	10.850	98.657	3.648	1.651	87.46	133	.71248
129	70-814	4.284	0.050	0.693	5.523	2.631	0.170	64.508	10.656	2.496	n.d.	7.098	98.109	1.511	2.605	92.67	104	.71248

Sample	Dept. No. of sample	Total Fe as Fe_2O_3	% MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	CO_2 (loss)	Σ	FeO	Fe_2O_3	ppm Rb	Sr	Sr^{87}/Sr^{86}
130	69-1192	2.177	0.060	0.268	26.358	0.905	0.188	15.656	3.690	13.712	0.929	35.951	99.813	0.838	1.186	37.65	142	.71049
131	69-1191	3.863	0.120	0.189	15.111	0.998	0.074	41.610	3.686	9.923	n.d.	22.975	98.549	3.201	0.304	34.53	136	.71949
132	70-811	3.359	0.088	0.277	14.824	1.171	0.083	41.590	4.677	9.914	n.d.	22.600	98.583	2.815	0.231	38.92	129	.71723
133	70-817	6.793	0.009	0.832	0.460	4.878	0.181	57.558	18.077	4.396	n.d.	2.870	96.054	4.070	2.270	272.91	20	n.d.
134	69-1217	5.597	0.010	0.928	0.337	6.401	0.163	54.697	20.388	5.334	n.d.	2.166	96.021	3.073	2.182	330.21	20	n.d.
135	69-1218	6.130	0.029	0.661	0.267	7.571	0.191	59.477	17.292	3.679	n.d.	2.540	97.807	3.174	2.603	283.64	50	.80818
136	70-809	0.268	0.018	0.011	26.904	0.143	0.029	9.050	0.824	20.216	0.038	42.560	100.061	0.137	0.116	9.10	285	.70905
137	69-1189	0.229	0.008	0.021	27.971	0.244	0.062	5.080	0.627	20.953	0.042	44.160	99.397	0.185	0.023	4.88	441	.70915
138	70-810	1.152	0.126	0.049	19.788	0.132	0.033	28.107	1.534	16.241	0.027	33.040	100.229	0.841	0.217	3.22	312	.71335
139	69-1190	1.649	0.069	0.023	29.474	0.056	0.078	2.201	0.520	19.991	0.043	45.650	99.754	0.100	1.583	4.81	228	.71168
140	69-1221	1.559	0.155	0.031	24.797	0.066	0.022	16.109	0.741	18.062	0.033	38.860	100.435	0.853	0.611	1.07	148	.71120
141	70-815	0.418	0.019	0.041	25.471	0.302	0.047	12.458	1.142	18.744	0.373	40.890	99.905	0.264	0.125	9.91	574	.71063
142	70-816	0.341	0.012	0.034	20.910	0.278	-	30.190	0.788	14.878	0.019	32.850	100.300	0.231	0.084	7.77	541	.71074
143	69-1215	0.477	0.019	0.041	26.192	0.439	0.064	10.980	1.496	18.751	0.304	41.330	100.093	0.257	0.191	10.40	696	.71060
144	69-1216	2.267	0.128	0.188	20.113	1.085	0.077	24.436	3.913	14.692	1.178	31.940	100.017	1.315	0.806	33.98	444	.71984
Amadeus Basin																		
145	70-352	0.340	0.138	0.002	29.213	0.073	0.045	3.886	0.124	20.813	0.041	45.430	100.085	0.132	0.193	0.78	35	.71276
146	70-341	0.449	0.208	0.032	29.023	0.116	0.036	4.012	0.520	19.932	0.040	45.180	99.548	0.332	0.080	2.59	35	.71007
147	70-820	0.678	0.059	0.013	28.907	0.299	0.046	8.311	0.618	18.352	0.037	42.820	100.140	0.290	0.356	4.64	51	.70872
148	70-353	0.290	0.077	0.029	48.899	0.149	0.035	5.442	0.593	2.761	0.028	41.090	99.393	0.124	0.152	2.56	53	.71161
149	70-311	0.182	0.011	0.017	30.830	0.324	0.030	16.103	0.546	13.157	0.025	38.460	99.685	0.036	0.142	7.01	39	.71070
150	70-821	0.113	0.005	0.020	51.491	0.256	0.058	6.517	0.693	0.188	0.022	40.770	100.133	0.051	0.056	3.85	112	.70751
151	70-332	0.112	0.035	0.005	48.727	0.088	0.034	0.859	0.264	5.445	0.026	44.200	99.822	0.044	0.063	0.62	179	.70744
152	70-822	0.947	0.048	0.051	25.254	0.668	0.046	14.057	1.200	17.959	0.041	39.330	99.601	0.390	0.514	16.17	68	.70715
153	70-333	0.526	0.048	0.011	20.868	0.096	0.033	31.690	0.437	14.555	0.032	32.310	100.606	0.259	0.238	4.09	58	.70767
154	70-334	0.881	0.026	0.009	53.954	0.062	0.041	2.078	0.211	0.119	0.014	42.420	99.815	0.045	0.831	1.09	38	.70751
155	70-335	0.754	0.035	0.063	46.932	0.693	0.062	13.004	1.127	0.341	0.016	36.820	99.847	0.050	0.698	10.48	35	.70849
156	70-823	0.340	0.073	-	36.939	0.074	0.028	12.539	0.149	10.033	0.055	39.920	100.450	0.178	0.142	0.88	62	.71010
157	70-336	2.546	0.066	0.139	44.810	1.296	0.144	11.376	1.887	0.624	0.043	35.610	98.541	0.032	2.510	17.90	77	.70889
158	70-337	0.160	0.048	-	8.402	0.028	0.011	74.899	0.148	4.584	n.d.	11.750	100.030	0.111	0.037	0.47	13	.70888
159	70-338	0.031	0.036	0.009	53.065	0.114	0.026	5.101	0.145	0.012	0.020	41.630	100.189	0.014	0.015	0.84	83	.70808
160	70-339	0.210	0.058	0.021	53.997	0.325	0.042	2.574	0.523	0.343	0.027	42.040	100.160	0.043	0.162	3.86	99	.70860
161	70-340	0.188	0.016	0.021	53.773	0.240	0.074	2.118	0.387	0.689	0.100	43.080	100.668	0.069	0.111	2.33	559	.70677

Sample	Dept. No. of sample	Total Fe as Fe_2O_3	MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	CO_2 (loss)	Σ	FeO	Fe_2O_3	Rb	Sr	Sr^{87}/Sr^{86}
		%														ppm		
Bangemall Group (Hamersley Basin)																		
162	W.A. R 1348	0.260	0.012	0.004	29.817	0.126	0.043	1.341	0.244	21.068	0.028	46.670	99.613	0.215	0.021	1.92	54	.70843
163	" R 1350	0.323	0.012	0.004	29.738	0.129	0.044	2.506	0.228	21.053	0.031	46.350	100.418	0.260	0.034	2.86	40	.70873
164	" R 1353	0.433	0.042	0.014	27.115	0.175	0.108	10.737	0.446	18.613	0.032	41.770	99.485	0.173	0.129	2.47	43	.70863
165	" R 1320	1.356	0.059	0.084	23.363	0.811	0.044	21.786	1.463	15.045	0.032	35.000	99.043	1.022	0.220	20.19	34	.75080
166	" R 1339	0.224	0.021	0.005	29.235	0.074	0.034	0.782	0.125	22.134	0.047	47.250	99.931	0.145	0.011	0.59	42	.70836
167	" R 1317	0.443	0.042	0.015	28.439	0.552	0.063	6.193	0.852	19.478	n.d.	44.030	100.107	0.329	0.077	11.47	46	.72037
168	" R 1309	0.506	0.051	0.004	29.322	0.051	0.036	3.800	0.148	20.585	0.025	45.610	100.138	0.403	0.058	1.53	53	.71440
Tasmania																		
169	70-824	0.666	0.022	0.052	30.826	0.710	0.059	32.861	1.432	4.048	0.052	28.590	99.318	0.457	0.158	9.88	54	.71434
McArthur Group																		
170	70-837	0.235	0.052	0.014	30.028	0.086	0.053	1.614	0.200	21.137	0.026	46.900	100.345	0.159	0.006	0.10	15	.70706
171	70-839	0.551	0.087	0.022	23.859	0.278	0.101	22.032	0.492	16.125	0.052	36.510	100.109	0.228	0.157	2.97	26	.70623
172	70-838	0.568	0.048	0.041	27.308	0.692	0.087	6.918	1.153	19.480	0.036	42.930	100.093	0.351	0.047	6.09	26	.70708
173	70-841	2.142	0.255	0.003	29.017	0.038	0.020	4.463	0.064	19.581	0.033	44.244	99.258	1.366	0.131	0.33	33	.70616
174	70-840	2.215	0.228	0.002	29.538	0.047	0.028	1.137	0.204	20.581	0.023	45.750	99.850	1.443	0.106	0.33	15	.70679
175	70-842	2.165	0.148	0.031	22.302	0.507	0.059	24.896	0.766	14.241	0.037	33.740	99.767	0.528	0.986	8.47	21	.71318
Mt Bruce Supergroup (Hamersley basin)																		
176	W.A. R 91	1.875	0.069	0.140	44.489	0.595	0.095	8.079	1.645	3.749	0.038	39.300	100.119	1.323	0.405	10.67	133	.70508
177	" R 90	1.302	0.179	0.044	29.092	0.502	0.096	4.880	1.235	18.950	0.054	43.450	99.784	0.792	0.422	11.32	29	.70942
178	" R 346	3.218	0.768	0.015	30.258	0.361	0.172	1.677	0.479	18.604	0.040	44.130	99.722	2.670	0.251	3.19	20	.74343
179	" R 344	2.126	0.468	0.142	17.818	1.959	0.058	34.379	3.338	11.306	0.047	26.520	98.161	1.653	0.289	32.70	12	.75047
180	" R 347	3.982	0.792	0.136	25.782	1.384	0.077	10.777	2.927	15.821	0.063	37.570	99.311	3.015	0.631	27.52	17	.72859
181	" R 345	2.320	0.484	0.005	31.304	0.158	0.063	0.931	0.359	18.648	0.028	45.250	99.550	1.892	0.217	0.19	11	.70723
182	" R 348	2.522	0.544	0.137	23.746	2.027	0.053	16.245	2.970	15.601	0.050	35.700	99.595	1.801	0.521	31.57	16	.72122
183	70-849	6.999	0.237	0.539	19.981	1.045	0.150	43.997	6.452	1.542	n.d.	17.614	98.556	3.693	1.202	50.82	47	.74098
Steep Rock Lake (Ontario, Canada)																		
184	Q.U.M. 53	0.240	0.245	0.008	51.167	0.073	0.035	7.653	0.098	0.160	0.012	40.110	99.801	0.125	0.101	0.07	391	.70206
185	" 54	0.356	0.178	-	53.514	0.078	0.040	1.670	0.131	0.914	0.031	42.720	99.632	0.251	0.077	0.32	578	.70198
Bulawayan Limestone (Rhodesia)																		
186		0.098	0.028	-	54.557	0.067	0.094	0.452	0.195	0.838	0.019	43.810	100.158	0.072	0.018	0.07	1107	.70165
187		0.078	0.029	0.012	55.192	0.034	0.070	0.182	0.148	0.493	0.009	43.850	100.098	0.031	0.044	0.35	1149	.70151

* Samples contained NaCl crusts. n.d. = not determined - = 0

Appendix No. 2 - Description of samples

No.	Age	Locality	Collected by	Description
1	Recent	Ephemeral Coorong E of Salt Lake	J. Veizer	Small gastropod shells
2	do	do	do	Arenaceous porous unlithified sediment composed mainly from broken gastropods
3	do	Jay Creek W of Alice Springs	do	Dark-grey nodular microcrystalline limestone (calcrete)
4	Late Miocene	Nasangalau, Lakemba Island, Fiji	J.B. Gill	White coral limestone (Futuna Limestone)-coral biolithite
5	Barremian-Aptian	Bobrovecká Valley, High Tatra Mts	J. Veizer	Dark organodetrital limestone-packed biomicrite
6	do	Kýcera, High Tatra Mts	do	do
7	do	Bobrovecká Valley, High Tatra Mts	do	Dark crinoidal limestone-crinoidal biomicrite
8	Late Neocomian	Zázrivá Valley, Krížna Nappe	do	Dark-grey marly pelagic limestones (Biancone type)-biomicrite
9	Neocomian	do	do	do
10	Malmian-Neocomian	Osobitá, High Tatra Mts	do	Light-grey muddy limestone-biomicrite
11	Oxfordian-Tithonian	Bobrovec, High Tatra Mts	do	Pink muddy limestones-biomicrite
12	Oxfordian-Kimmeridgian	Osobitá, High Tatra Mts	do	do
13	Doggerian-Malmian	Zázrivá Valley, Krížna Nappe	do	Red siliceous nodular limestone-siliceous micrite
14	Bathonian	Bobrovecká Valley, High Tatra Mts	do	Pink crinoidal limestone-crinoidal biosparite
15	Bajocian-Bathonian	Rozpadlý Grúň, High Tatra Mts	do	do
16	Bajocian	Bobrovecká Valley, High Tatra Mts	do	Grey crinoidal limestone-crinoidal biosparite
17	Rhaetian	Zázrivá Valley, Krížna Nappe	do	Dark-grey coquina-crinoidal limestone-crinoidal biosparite to oosparite
18	Norian	Silická Brezová, Gemeridy Unit	do	Red muddy limestone (Hallstat Limestone)-biomicrite
19	do	Kvačianska Valley, Choč Nappe	do	Light-grey late diagenetic dolomite (Hauptdolomite)-dolsparite to dolmicrite
20	Karnian-Norian	Zázrivá Valley, Krížna Nappe	do	Grey fine-grained sheet marly early diagenetic dolomite (Keuperdolomite)-dolmicrite
21	(Anisian?)-Karnian-Norian	Osobitá, High Tatra Mts	do	Grey sheet marly early diagenetic dolomite-dolmicrite
22	Karnian-Norian	Spiš-Michalová Valley, High Tatra Mts	do	Variegated sheet marly early diagenetic dolomite-dolmicrite
23	(Ladinian?)-Karnian-Norian	Kýcera, High Tatra Mts	do	Grey sheet marly early diagenetic dolomite-dolmicrite
24	Karnian	Silická Brezová, Gemeridy Unit	do	Light-grey organodetrital, mainly crinoidal, limestone-biosparite-biomicrite

No.	Age	Locality	Collected by	Description
25	Karnian	Silica Plateau, Gemeridy Unit	J. Veizer	Light-grey muddy limestone-micrite
26	Ladinian	Kvačianska Valley, Choč Nappe	do	Grey massive late diagenetic dolomite (Choč Dolomite)-dolsparite
27	do	Plešivec Plateau, Gemeridy Unit	do	Light-grey organodetrital limestone-algal biopelmicrite
28	do	do	do	Light grey organodetrital limestone-coral biomicrite
29	do	Vrátna Valley, Choč Nappe	do	Grey late diagenetic dolomite (Choč Dolomite)-dolsparite
30	Late Anisian	Plešivec Plateau, Gemeridy Unit	do	Dark-grey fine-grained limestone, partly recrystallised-sparite
31	do	do	do	Light-grey fine-grained dolomitic limestone-micrite
32	do	do	do	Light-grey fine-grained limestone-micrite
33	do	Rozpadlý Grúň, High Tatra Mts	do	Brown-grey massive limestone-micrite
34	do	Osobitá, High Tatra Mts	do	do
35	do	do	do	do
36	do	do	do	do
37	do	Plešivec Plateau, Gemeridy Unit	do	Light coloured organodetrital limestone-algal biomicrite to biosparite
38	Early Anisian	Rozpadlý Grúň, High Tatra Mts	do	Grey muddy limestones (Würmlikalk)-micrite
39	do	Plešivec Plateau, Gemeridy Unit	do	Dark fine-grained limestone (Gutenstein Limestone)-micrite
40	do	do	do	do
41	Late Campilian-Early Anisian	do	do	Yellow porous limestone with rhombs of early diagenetic dolomite (Rauhwacken)-sparite
42	Early to Middle Kazanian	Gerringong, Sydney Basin	K.S.W. Campbell	Ingerella sp. (Gerringong Volcanics)
43	do	do	do	"Spirifer" convolutus (Gerringong Volcanics)
44	Late Artinskian	Homevale, Qld	do	Neospirifer sp. (Tiverton Formation)
45	do	do	do	Taeniothareus subquadratus (Tiverton Formation)
46	do	do	do	Strophalosia sp. (Tiverton Volcanics)
47	Early to Middle Artinskian	Springsure, Qld	do	"Spirifer" sp. (Cattle Creek Formation)
48	Westphalian	Barrington, N.S.W.	do	Neospirifer sp. (Levipustula Beds)
49	do	do	do	do
50	Middle Late Viséan	Hilldale, N.S.W.	do	Leptagonia cf. analoga (Wallaringa Formation)

No.	Age	Locality	Collected by	Description
51	Early Late Viséan	Wallarobba Region, N.S.W.	K.S.W. Campbell	Delepinea aspinoza (Wirragulla Beds)
52	do	do	do	Unispirifer striatoconvolutus (Wirragulla Beds)
53	Tournasien	Ningbing Homestead (Bonaparte Gulf Basin), W.A.	J.J. Veevers	Skeletal sparry silty lump limestone
54	Famenian	Surprise Creek Gorge (Bonaparte Gulf Basin), W.A.	do	Sparry lump limestone (Ningbing Limestone)
55	do	do	do	Skeletal sparry algal micrite (Ningbing Limestone)
56	do	S tip of Ningbing Range (do), W.A.	do	Sparry algal micrite limestone (do)
57	do	do	do	Sparry lump limestone (do)
58	Frasnian	Westwood Creek area (do), W.A.	do	Skeletal solenopore sparry lump limestone (Westwood Member)
59	Late Emsian	Cavan Station, N.S.W.	J. Veizer	Grey laminated stromatolitic silty limestone (Cavan Bluff Limestone)-arenaceous micrite
60	do	do	do	do
61	do	do	do	do
62	do	do	do	do
63	Middle Ludlovian	Rainbow Hill near Yass, N.S.W.	do	Dark-grey fine-grained limestone-arenaceous micrite
64	do	Yass River near Rainbow Hill, N.S.W.	do	Light-grey coral (Favosites) limestone (Hume Limestone)-coral biolithite
65	do	do	do	Light-grey crinoidal limestone (Hume Limestone) crinoidal biosparite
66	do	Derengolong Creek near Yass, N.S.W.	do	Grey coarse-grained crinoidal limestone (Barrandella Shale)-crinoidal biomicrite
67	do	do	do	Dark-grey fine-grained crinoidal limestone (Bowspring Limestone)-algal and crinoidal biomicrite
68	Early Ludlovian	do	do	Light-grey organodetrital limestone-algal and crinoidal biosparite
69	do	do	do	Dark-grey organodetrital limestone-biomicrite
70	Late Ordovician	Crossing of Lord and Lawrence Creek Roads, Tas.	do	Black fine-grained bedded marly limestone (Gordon Limestone)-micrite
71	do	Lord Road, Tas.	do	Dark-grey to black muddy limestone (Gordon Limestone)-crinoidal micrite
72	do	do	do	do

No.	Age	Locality	Collected by	Description
73	Middle Ordovician	Crossing of Lawrence Creek and Eden Creek Roads, Tas.	J. Veizer	Dark-grey to black massive muddy limestone (Gordon Limestone)-biomicrite
74	do	do	do	do
75	do	do	do	do
76	do	Junction of Lords and Westfield Roads, Tas.	do	Dark-grey fine-grained limestone (Gordon Limestone)-crinoidal biomicrite
77	do	do	do	do
78	do	Florentine Valley, Tas.	M.R. Banks	Dark-grey fine-grained organodetrital limestone (Gordon Limestone)-biomicrite
79	do	Mole Creek, Tas.	do	do
80	Early Ordovician	Crossing of Florence Road and Road No. 9, Tas.	J. Veizer	Dark-grey to black massive muddy and nodular clayey limestone (Gordon Limestone)-micrite
81	do	do	do	do
82	Early Late Cambrian	Ellery Creek W of Alice Springs, N.T.	do	Brown-grey fine-grained partly recrystallised limestone (Geyder Limestone)-recrystallised micrite
83	do	do	do	Grey fine-grained oolitic and organodetrital limestone (Goyder Limestone)-biomicrite and oomicrite
84	do	do	do	Yellow-grey medium-grained limestone (Goyder Limestone)-intrasparite
85	Late Middle Cambrian	do	do	Dark-grey oolitic limestone (Jay Creek Limestone)-oointrasparite
86	do	do	do	Dark-grey fine-grained laminated limestone (Jay Creek Limestone)-intramicrite
87	do	Jay Creek W of Alice Springs, N.T.	do	Yellow-grey fine-grained dolomitic algal limestone (Jay Creek Limestone)-dolomitic algal micrite
88	do	do	do	Yellow-grey fine-grained laminated limestone (Jay Creek Limestone)-oointrasparite
89	do	do	do	Grey fine-grained oolitic limestone (Jay Creek Limestone)-oosparite
90	Middle Cambrian	Ellery Creek W of Alice Springs, N.T.	do	Light-grey fine-grained sheet early diagenetic dolomite (Hugh River Shale)-dololutite
91	do	do	do	Grey fine-grained arenaceous algal limestone (Hugh River Shale)-arenaceous algal micrite
92	do	50 miles E of the Urandangi, Qld, 139 00', 22 00'.	P.J. Cook	Grey fine-grained organodetrital limestone (Quita Formation)
93	do	do	do	Yellow fine-grained laminated (algal?) limestone (Quita Formation)

No.	Age	Locality	Collected by	Description
94	Middle Cambrian	35 miles E of the Lawn Hill Homestead, Qld, 138 00',18 30'	P.J. Cook	Light-grey medium-grained late diagenetic dolomite (Currant Bush Limestone)
95	do	do	do	Yellow-grey coarse-grained arenaceous late diagenetic dolomite (Currant Bush Limestone)
96	do	50 miles ESE from Urandangi, Qld, 139 00',21 45'	do	Yellow fine-grained early diagenetic dolomite (Thorntonia Limestone)-microcrystalline dolomite
97	do	do	do	Yellow fine-grained late diagenetic? dolomite (Thorntonia Limestone)-dolsparite
98	do	Victoria River Downs, N.T.	M.C. Brown	Grey fine-grained microcrystalline dolomitic limestone (Montejinni Limestone)
99	do	Wave Hill, N.T.	do	Yellow-grey massive dolomitic limestone (Montejinni Limestone)
100	do	Brachina Gorge, S.A.	J. Veizer	Grey nodular and laminated clayey limestone (Wirrealpa Limestone)-stromatolitic? micrite
101	do	Wirrealpa Creek, S.A.	do	Grey fine-grained organodetrital limestone (Wirrealpa Limestone)-archaeocayathid micritic biolithite
102	do	do	do	Creamy-red fine-grained organogenic, partly recrystallised limestone (Wirrealpa Limestone)-archaeocyathid biolithite
103	do	do	do	Variegated medium-grained organogenic limestone (Wirrealpa Limestone)-archaeocyathid biolithite
104	Early Cambrian	Old Wirrealpa Springs, S.A.	do	Creamy-grey clayey limestone (Pararra Limestone)-micrite
105	do	do	do	Red fine-grained silty limestone (Pararra Limestone)-arenaceous intramicrite
106	do	do	do	Black fine-grained arenaceous detrital limestone (Pararra Limestone)-arenaceous intramicrite
107	do	Brachina Gorge, S.A.	do	Red fine-grained laminated arenaceous late diagenetic dolomite (Wilkawillina Limestone)-arenaceous dolsparite
108	do	do	do	Dark-grey massive late diagenetic calcitic dolomite (Wilkawillina Limestone)-predominantly dolsparite
109	do	S of Warragee Bore, S.A.	do	Grey fine-grained recrystallised limestone (Wilkawillina Limestone)-crystalline limestone
110	do	do	do	do
111	Marinoan	Brachina Gorge, S.A.	do	Creamy-grey muddy laminated limestone (Wonoka Formation)-micrite
112	do	do	do	Red massive fine-grained early ? diagenetic dolomite (Nuccaleena Formation)-dolmicrite
113	do	Depot Creek, S.A.	do	Red fine-grained laminated dolomitic silstone (Willochra Subgroup)
114	do	do	M.V. Preiss	Green arenaceous fine-grained dolomitic limestone with stromatolites (Willochra Subgroup)-dolomitic micrite

No.	Age	Locality	Collected by	Description
115	Marinoan	Brachina Gorge, S.A.	J. Veizer	Red fine-grained nodular silicified algal limestones (Trezona Formation)-micrite
116	do	do	do	Grey medium-grained silicified stromatolitic limestone (Trezona Formation)-predominantly sparite
117	do	do	do	Red fine-grained algal and oolitic limestone (Trezona Formation)-algal bio-oomicrite
118	do	do	do	Dark fine-grained arenaceous oolitic limestone (Etina Limestone)-arenaceous oosparite
119	do	do	do	do
120	Sturtian	Depot Creek, S.A.	do	Green and grey fine-grained laminated nodular dolomitic limestone, partly silicified (Brighton Limestone eq.)-alteration of algal micrite and sparite laminae
121	do	do	do	Creamy-red nodular fine-grained oolitic limestone (Brighton Limestone eq.)-algal bioosparite
122	do	do	do	Red nodular fine-grained oolitic limestone (Brighton Limestone eq.)-algal oobiosparite
123	do	Brighton Quarry, S.A.	do	Black fine-grained laminated calcareous silstone (Brighton Limestone)
124	do	do	do	Red fine-grained nodular and laminated calcareous silstone (Brighton Limestone)
125	do	do	do	Black fine-grained calcareous silstone (Brighton Limestone)
126	do	do	do	Vein of secondary sparry calcite in sample No. 125
127	do	Depot Creek, S.A.	do	Dark-grey fine-grained laminated calcareous silstone (Tapley Hill Formation)
128	do	do	do	do
129	do	S of Orapparina, S.A.	do	do
130	do	Depot Creek, S.A.	do	Black laminated muddy early diagenetic dolomite with cherts (Tindelpina Shale Member)-silicitic dolpelmicrite
131	do	do	do	Dark-grey fine-grained dolomitic silstone (Apilla Tillite) with chert layers
132	do	do	do	do
133	Torrensian	Broughton River near Spalding, S.A.	do	Dark-grey dolomitic mudstone (Auburn Dolomite)
134	do	do	do	do
135	do	do	do	do
136	do	Depot Creek, S.A.	do	Black muddy early diagenetic dolomite with cherts (Skillogalee Dolomite)-dolmicrite
137	do	do	do	do
138	do	do	do	do

No.	Age	Locality	Collected by	Description
139	Torrensian	Depot Creek, S.A.	J. Veizer	Grey creamy cavernous dolomite (Rauhwacken) (Skillogalee Dolomite)-dolmicrite
140	do	do	M.V. Preiss	Variegated and red fine-grained early diagenetic dolomite with stromatolites and cherts (Skillogalee Dolomite)-stromatolitic silicitic micrite
141	Willouran	Carrieton, S.A.	J. Veizer	Black muddy sheet early diagenetic dolomite with sporadic cherts (River Wakefield Group)-dolmicrite
142	do	do	do	do
143	do	do	do	do
144	do	do	do	Black laminated fine-grained arenaceous early diagenetic dolomite (River Wakefield Group)-dolmicrite
145		Jay Creek, N.T.	do	Yellow-grey sheet muddy early diagenetic dolomite (Pertatataka Formation)-algal dolmicrite, partly recrystallised
146		Ellery Creek, N.T.	do	Grey sheet muddy early diagenetic dolomite (Pertatataka Formation)-microcrystalline dolomite
147		Jay Creek, N.T.	do	Fine-grained dark-grey early diagenetic sheet dolomite (Bitter Springs Formation)
148		do	do	Variegated coarse-grained calcite with stromatolites and cherts (do)-sparite
149		do	do	Creamy fine-grained calcite dolomite with stromatolites and cherts (do)-dolsparite
150		do	do	Dark-grey muddy limestone (do)
151		do	do	Dark-grey muddy laminated stromatolitic limestone, partly recrystallised (do)
152		Ellery Creek, N.T.	do	Black muddy sheet argillaceous early diagenetic dolomite (do)
153		do	do	Grey laminated microcrystalline sheet early diagenetic dolomite with stromatolites and cherts (do)
154		do	do	Yellow fine-grained cavernous limestone (Rauhwacken) (Bitter Springs Formation)
155		do	do	Red medium-grained arenaceous partly recrystallised nodular limestone (Bitter Springs Formation)
156		do	do	Grey medium-grained weakly recrystallised limestone (do)
157		do	do	Red argillaceous stromatolitic limestone (do)-micrite
158		do	do	Laminated stromatolitic dolomitic silicite (do)
159		do	do	Grey laminated stromatolitic muddy limestone with cherts (do)-micrite

No.	Age	Locality	Collected by	Description
160		Ellery Creek, N.T.	J. Veizer	Variegated partly recrystallised microcrystalline stromatolitic limestone (Bitter Springs Formation)
161		do	do	Black fine-grained limestone with veins of secondary calcite (do)
162		115 39', 22 32', W.A.	A.F. Trendall	Grey partly recrystallised medium grained early diagenetic dolomite (Bangemall Group)-algal? intradolsparite
163		do	do	Grey partly recrystallised early diagenetic dolomite (do)-predominantly dolmicrite
164		115 41', 22 31', W.A.	do	Fine-grained slightly recrystallised early diagenetic dolomite with cherts (do)-dolsparite
165		115 42', 22 56', W.A.	do	Middle-grained early diagenetic dolomite with cherts (do)
166		115 48', 22 52', W.A.	do	Fine-grained slightly recrystallised early diagenetic dolomite (Bangemall Group)-predominantly dolmicrite
167		115 43', 22 56', W.A.	do	Middle-grained partly recrystallised early diagenetic dolomite (do)
168		115 38', 23 05', W.A.	do	Middle-grained recrystallised mosaic dolomite with cherts (do)
169	Carpentarian?-Adelaidean?	Gordon River Road near Tim Shea, Tas.	J. Veizer	Black massive nodular fine-grained limestone (Clarke Series)
170	Carpentarian	11.5 miles NW of Balbirini Homestead, Bauhinia Downs sheet, Qld	M.C. Brown	Grey fine-grained early diagenetic dolomite (Reward Dolomite)
171	do	do	do	Dark-grey fine-grained early diagenetic dolomite with cherts, limonitic layers and veins of secondary calcite (Reward Dolomite)
172	do	Top Crossing, Bauhinia Downs sheet, Qld	do	Pink muddy early diagenetic dolomite with aragonitic? pseudomorphs (Cooley Member)
173	do	Bald Hill, Bauhinia Downs sheet, Qld	do	Grey and pink muddy early diagenetic dolomite (Mitchell Yard Member)-dolmicrite
174	do	2 miles W of old McArthur River Homestead, Bauhinia Downs sheet, Qld	do	Dark-grey muddy early diagenetic dolomite (Mara Dolomite)-dolmicrite
175	do	6 miles W of Leila First Crossing, Bauhinia Downs sheet, Qld	do	Yellow fine-grained laminated early diagenetic arenaceous dolomite (Leila Sandstone)-dolmicrite
176	Nullaginian	116 32', 22 28', W.A.	A.F. Trendall	Fine-grained recrystallised limestone with cherts (Duck Creek Dolomite)
177	do	do	do	Fine to middle-grained mosaic dolomite (Duck Creek Dolomite)
178	do	116 27', 21 51', W.A.	do	Middle to coarse-grained dolomite (Wittenoom Dolomite)

No.	Age	Locality	Collected by	Description
179	Nullaginian	119 10', 22 52', W.A.	A.F. Trendall	Middle-grained dolomite with cherts (Wittenoom Dolomite)
180	do	116 27', 21 51', W.A.	do	Banded middle-grained dolomite with cherts (do)
181	do	117 47', 22 45', W.A.	do	Middle to coarse grained dolomite with cherts (do)
182	do	117 48', 21 55', W.A.	do	Middle to coarse-grained dolomite with cherts and ankeritic? layers (Wittenoom Dolomite)
183	do	Mt Herbert, Yaraloola sheet, W.A.	M.R. Walter	Fine-grained algal silicite (Pillingani Tuff)
184	Archaean	Steep Rock Lake, Ontario, Canada	A.W. Jolliffe	Dark-grey fine-grained massive limestone, partly recrystallised
185	do	do	do	Grey fine-grained massive and banded limestone
186	do	Huntsman Lime Works Quarry near the Turk Mine, 33 miles NNE of Bulawayo, Rhodesia	C.C. Smith	Black fine-grained slightly recrystallised limestone with calcitic eyes (Bulawayan Limestone)
187	do	do	do	do

Appendix 3

CARBONATE ROCKS OF THE WESTERN CARPATHIANS AND THEIR DIAGENETIC MODEL

3.1 THE DIAGENETIC MODEL

The Mesozoic carbonate rocks of the Western Carpathians (Table 11) may be divided according to their Sr concentrations into two groups (fig. 52).

I shall try to explain the Sr distribution on the facies model presented in Table 12. The types of sediments and their diagenetic history, for a cross-section lagoon - algal bank - deeper neritic to shallow pelagic - deep sea, are based on the discussion of diagenesis presented by Fairbridge (1967b), Zankl (1969), Veizer (1970a) and Veizer et al. (1971).

The cement and/or matrix precipitating in the presence of solutions derived from sea water is mainly high-Mg calcite or aragonite (cf. Füchtbauer, 1969). Although the relative importance of these two minerals is not clear, it seems that aragonite is the major cementing mineral in environments with high Mg/Ca ratios of pore solutions, whereas high-Mg calcite is typical for environments with Mg/Ca of pore waters similar to that of sea water (DeGroot, 1969; Taylor and Illing, 1969; Friedman, 1968). Müller et al. (1971) showed that in the lacustrine environments aragonite is the precipitated mineral at $^{m}Mg/^{m}Ca$ ratios > 25, aragonite and/or high-Mg calcite at ratios between 1 and 25 and low-Mg calcite at ratios < 1.

The first group consists of populations with Sr content $\sim$ 600-700 ppm and the second group has Sr concentrations $\sim$100-250 ppm. The dolomites will be discussed later in the text. The differences between the means of these two groups are statistically significant at the 99% confidence level. The two groups of limestones were previously explained as a result of their different original mineralogy (Veizer et al., 1971). The

Table 11.

Petrological characteristics of the rock populations

No.	Description	Age	Classification	Composition of the framework	Supposed original mineralogical composition: 1,framework; 2,cement and/or matrix; 3, prevailing for the whole rock	Character and composition of the Insoluble Residue: 1, fraction > 2 μ 2, fraction < 2 μ
	Mantle Series of the High-Tatra Mts.					
1	marly fine-grained early diagenetic dolomites	Triassic	dolmicrite		1 - 0 2 - aragonite 3 - "	1 - 0 2a - illite, chlorite c - kaolinite
2	fine-grained limestone (+ 1 sample of cavernous dolomite) see Veizer (1970)	Anisian (Triassic)	micrite		1 - 0 2 - aragonite 3 - "	1 - 0 2a - illite b - chlorite
3	dolomitised laminated and recrystallised limestone	Early Anisian (Triassic)	dolomitised coral? biolithite	a- corals?	1 - aragonite? 2 - ? 3 - aragonite?	not determined, very low
4	variable arenaceous organodetrital and oolitic limestones with cherty layers	Rhaetian - Liassic	mainly arenaceous biomicrite and oomicrite	a- crinoid ossicles, oolites b- gastropods, pelecypods, foraminifera, bryozoa, algae c- corals, ostracods	1 - high-Mg calcite and aragonite 2 - high Mg calcite? 3 - calcite (high-Mg)	1a - quartz, quartzite b - feldspar, muscowite, haematite, limonite c - pyrite, zircon, rutile 2a - illite b - montmorillonite
5	crinoidal limestones	Bajocian - Bathonian (Doggerian)	crinoidal biosparite	a- crinoid ossicles	1,2,3 - high-Mg calcite	1a - quartz, quartzite c - zircon, rutile, chlorite, sphene, haematite 2a - illite b - chlorite c - kaolinite
6	fine-grained deeper neritic to pelagic limestones with haematitic pisolites	Late Bathonian and Callovian (Doggerian)	biomicrite	a- foraminifera, "Posidonia" fibres b- small gastropods, crinoid ossicles, pelecypods	1 - low-Mg calcite 2 - high-Mg calcite? 3 - calcite	1 - 0 2a - illite b - chlorite
7	fine-grained pelagic limestones	Malmian - Neocomian	biomicrite and pelmicrite	a-"protoglobigerina", foraminifera b- crinoid ossicles, ostracoda, small gastropods, pelecypods, Tintinidae, "Posidonia"fibres , spicules of spongae	1 - low-Mg calcite 2 - high-Mg calcite? 3 - calcite	1 - 0 2a- illite, chlorite
8	fine-grained light-coloured organodetrital limestones	Barremian - Aptain (Urgonian)	mainly packed biomicrite	a- pelecypods, Orbitolina b- gastropods, crinoid ossides, foraminifera, brachyopods, corals, echinoid spines, spongae, algae	1 - calcite > aragonite 2 - high-Mg calcite 3 - calcite	1 - 0 2 - illite
9	dark-grey to black fine-grained limestone with black cherts.	(Neocomian) - Barremian - Aptian	crinoidal biomicrite micrite	a- crinoid ossicles b- bryozoa, gastropods foraminifera, pelecypods, orbitolina, algae	1 - calcite 2 - aragonite 3 - aragonite >> calcite	1a - quartz 2a - illite b - kaolinite, chlorite
	Slovak Karst					
10	light-grey massive organodetrital algal limestones	Late Anisian and Ladinian (Triassic)	mainly algal biomicrites	a-"Dasycladaceae" b- molluscs, corals	1,2,3 high-Mg calcite	1 - 0 2 - not determined
11	nodular fine-grained limestones with cherts (Schreyeralm Limestones)	Late Anisian (Triassic)	micrites - biomicrites	b- spicules of spongae, radiolaria, pelecypods, brachiopods and ammonites	1 - calcite? 2 - high-Mg calcite? 3 - calcite?	1 - 0 2 - not determined

0 = not present
a = abundant; b = present ; c = rare

Figure 52. Scatter diagram of (Sr/Ca) x 10^3 vs. (Mg/Ca) x 10^2.
Explanations:
Populations 1-11 as in Table 11. Additional populations with number of analyses in parenthesis: 12 (12) - light-grey organodetrital (algal) and crinoidal limestones, Anisian-Karnian of the Krížna Nappe and Gemeridy Units, 13 (5) - Early Anisian Gutenstein or Annaberg Limestone of the Choč Nappe and Gemeridy Units, 14 (6) - Liassic Borinka Limestones of the Malé Karpaty Mantle Series, 15 (5) - Tithonian-Aptian pelagic marly limestones of the Krížna Nappe, 16 (3) - Triassic early diagenetic dolomites of the Krížna Nappe and High Tatra Mantle Series, 17 (4) - Triassic late diagenetic dolomites of the Choč Nappe, 18 (12) - Triassic Vysoká Limestones of the Krížna Nappe, 19 (6) - dark-grey Anisian Havranica Limestones of the Choč Nappe, 20 (11) - Triassic Vápenica (=Raštún) Limestones of the Choč Nappe, 21 (36) - Late Anisian Jablonica Limestones of the Choč Nappe, 22 (10) - Ladinian Veterník Limestones of the Choč Nappe, 23 (4) - Late Anisian to Early Ladinian light-grey Havranica Limestones of the Choč Nappe, 24 (20) - Ladinian Nedzov Limestones of the Choč Nappe.

The dot-dash line represent preferred arbitrary division line for the two (four) facial groups.

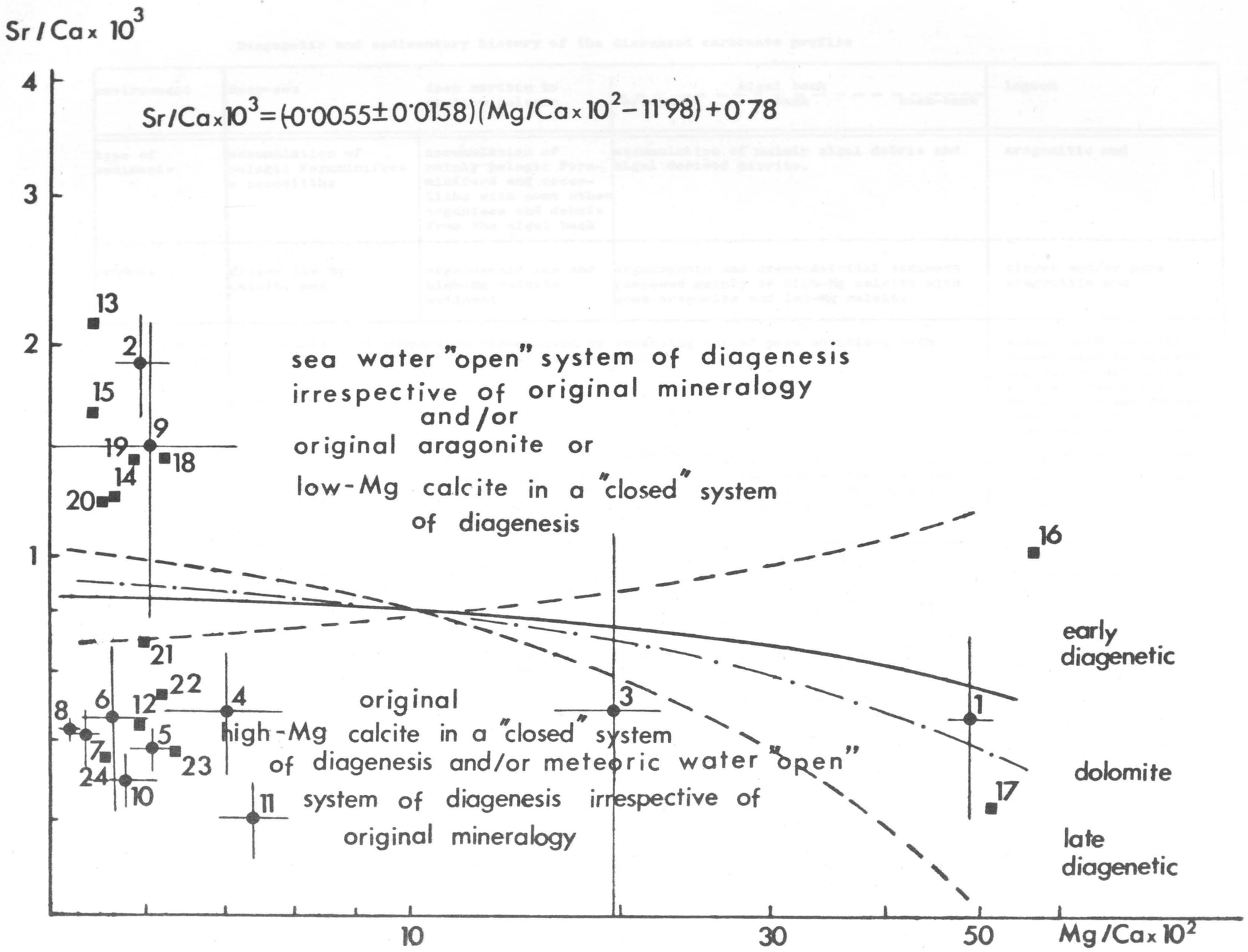

Sr / Ca x 10^3
Sr/Ca x 10^3 = (-0·0055 ± 0·0158)(Mg/Ca x 10^2 − 11·98) + 0·78
4
3
2
1
13
2
15
9
19
18
14
20
sea water "open" system of diagenesis irrespective of original mineralogy and/or original aragonite or low-Mg calcite in a "closed" system of diagenesis
16
early diagenetic
21
22
6
12
4
3
1
8
5
7
23
24
10
11
original high-Mg calcite in a "closed" system of diagenesis and/or meteoric water "open" system of diagenesis irrespective of original mineralogy
dolomite
17
late diagenetic
10
30
50
Mg / Ca x 10^2

Table 12.

Diagenetic and sedimentary history of the discussed carbonate profile

environment		deep-sea	deep neritic to shallow pelagic	algal bank: fore-bank	algal bank: bank	algal bank: back-bank	lagoon
type of sediments		accumulation of pelagic Foraminifera + coccoliths	accumulation of mainly pelagic Foraminifera and coccoliths with some other organisms and debris from the algal bank	accumulation of mainly algal debris and algal derived micrite.			aragonitic mud
product		clayey low-Mg calcite mud	organogenic low and high-Mg calcite sediment	organogenic and organodetrital sediment composed mainly of high-Mg calcite with some aragonite and low-Mg calcite			clayey and/or pure aragonitic mud
syndiagenesis	initial stage	mainly void compaction accompanied by squeezing out of pore solutions with chemistry similar to sea-water					mainly void compaction accompanied by squeezing out of entrapped pore solutions with high Mg/Ca ratio and subsequent formation of early diagenetic dolomites
		cementation mainly by high-Mg calcite					cementation by aragonite
	product	clayey low-Mg calcite mud with low porosity	grain supported fabric of mainly high-Mg calcite with porosity 40-50%	grain supported fabric with low clay content and mainly high-Mg calcite mineralogy with 40-50% porosity			aragonitic clayey mud with low remaining porosity
	early burial stage	grain compaction by pressure solution and squeezing out of remaining pore solutions	some grain compaction accompanied by squeezing out pore solutions	formation of late diagenetic dolomites			grain compaction by pressure solution accompanied by squeezing out of pore solutions with high Mg/Ca ratios into the permeable bank body
			lithification by conversion of metastable minerals into stable ones (mainly high-Mg calcite into low-Mg calcite)				lithification by conversion of aragonite into low-Mg calcite.
			formation "in situ" of late diagenetic dolomites by Mg released during the conversion				
	product	compact clayey fine-grained limestone with very low remaining porosity	cemented limestones with some original porosity	cemented limestones with some original porosity and layers of late diagenetic dolomites	late diagenetic dolomites with secondary porosity		compact fine-grained limestones with intercalations of early diagenetic dolomites and very low remaining porosity
anadiagenesis		additional cementation by pore solutions (low-Mg calcite?)					
		C O M P A C T C A R B O N A T E R O C K S					
epidiagenesis		epidiagenetic changes not specified					

assumptions at that time were based only on the matrix and organogenic skeletons, mainly because cementation in the marine environment was believed to be confined to a very shallow depth, with aragonite as a cementing mineral. However, the porosity and permeability of organodetrital facies is very high so that cement can be more abundant than framework. Since then, there has also been a substantial accumulation of data supporting the role of high-Mg calcite as a cementing mineral in marine environments. The interpretation here is thus based on these additional data.

Carbonate sediments are changed into carbonate rocks mainly through transformation of unstable carbonate minerals into stable ones. This transformation is caused by multiple solution-precipitation processes in the presence of a fluid phase (pore water), rather than by a solid state inversion (see Chapter 9). At this stage of discussion I prefer not to specify the volume and origin of this fluid phase. The solution-precipitation process must be confined to a very small scale to account for the preservation of textural features as well as for the partition of Sr between organic textures, matrix and cement as discussed in Chapter 9. This means that dissolution of an unstable phase is accompanied by precipitation of a stable phase, almost in the same place (diffusive processes of solution alteration) (Sippel and Glover, 1964). If so, the chemical composition of the fluid is governed mainly by the composition of the dissolved phase. The diagenetic system discussed above will be referred to in the following discussion as a "closed" system, whereas a system in which the composition of pore fluids is not substantially influenced by the dissolved metastable phase (e.g. dolomitization) will be referred to as an "open" system of diagenesis. The latter would cause greater obliteration of original textures and formation of recrystallization phenomena.

The "closed" system of diagenesis defined in this manner might act as a more or less open system with respect to pore solution, whereas the partition of Sr into a stable precipitated phase is governed by the Sr content and mineralogical mode of the original phase. This means that the "loss" of Sr is not random, but proportional. However, on a long term basis even multiple "closed" system alteration may lead to virtually an "open" system of diagenesis, compared with its initial stage. The selection of algal bank is intentional, because it is not clear to me, if an aragonitic framework (e.g. corals) would cause nucleation of aragonite cement in spite of sea-water composition of pore solutions.

Discussing the Sr behaviour within the lagoonal environment, it is not very difficult to explain the high Sr concentrations. Accepting the reasoning described by Kinsman (1969), the original aragonitic composition (~9000 ppm of Sr), high Sr/Ca ratios of pore solutions, low permeability and higher clay content may easily account for Sr concentrations of the final phase~1000 ppm. Allowing for a degree of "open" system diagenesis Sr concentrations~600-700 ppm are very reasonable. It is probable that in such sediments a very high degree of an "open" system diagenesis (e.g. continental waters) would be required to produce a final phase with Sr content~300 ppm.

In the case of algal bank and bank derived sediments the mineralogy of the framework is determined by its organic composition (high-Mg calcite of algae, some aragonite and low-Mg calcite of other organisms). Such sediments are cemented mainly by high-Mg calcite (cf. Alexandersson, 1969; Ginsburg et al., 1967; Winland, 1968 etc.) with Sr concentrations 400-1000 ppm (Land and Goreau, 1970). All metastable phases become unstable during the early burial stage of syndiagenesis and as long as they are present and being dissolved (Kinsman, 1969) diagenetic calcite will continue

to be precipitated in spite of supersaturation of the pore fluid with respect to calcite. Assuming a "closed" system of diagenesis, the above process would lead to a decrease of $({}^{m}Sr^{2+}/{}^{m}Ca^{2+})_{L}$ and precipitation of calcites with much lower Sr concentrations. The value of $({}^{m}Sr^{2+}/{}^{m}Ca^{2+})_{L}$ for sea-water is 0.86×10^{-2} and for continental waters 0.32×10^{-2} (Kinsman, 1969), whereas the values of high-Mg calcites with Sr concentrations 400-1000 ppm are 0.046 - 0.11×10^{-2}. This indicates that their conversion leads to a decrease of $({}^{m}Sr^{2+}/{}^{m}Ca^{2+})_{L}$ of the pore solutions. The value $({}^{m}Sr^{2+}/{}^{m}Ca^{2+})_{L}$ required for the precipitation of low-Mg calcites with 200-400 ppm of Sr is $0.16\text{-}0.32 \times 10^{-2}$. This is within the limits of solutions derived by dissolution of high-Mg calcites in sea-water or meteoric water. Mg released during this conversion may account for late diagenetic dolomitic layers, which may form $\sim\frac{1}{3}$ of the whole sequence.

A similar calculation might be applied to sediments of deeper neritic to shallow pelagic environments. The proportion of stable low-Mg calcites due to the increased concentrations of pelagic foraminiferas and coccoliths is higher than in the previous case. These sediments are also cemented mainly by high-Mg calcite (Friedman, 1964; Milliman, 1966; Fischer and Garrison, 1967 etc.) and they may have low Sr concentrations even with a "closed" system of diagenesis. It is not necessary to invoke a continental water influence, which might not be available in such environments.

The situation is slightly different in a deep sea environment. Due to the increased solubility of carbonates with depths, the falling carbonate skeletons are dissolved. This affects mainly the metastable phases and the carbonate in the bottom sediments is mainly stable low-Mg calcite. Because of the stability of the carbonates and the generally high clay content of such sediments, the main diagenetic process is pressure solution of grain edges, and the cores are largely unaltered. This may account for the high

Sr concentrations of such sediments (≥500 ppm). This explanation was first discussed by Flügel and Wedepohl (1967) in the case of pelagic Oberalm Limestones (Malmian; Eastern Alps).

It is obvious that due to variations in the relative importance of "closed" and "open" systems of diagenesis each population may display a somewhat variable pattern of Sr distribution. Also, the presence of continental waters during diagenesis would influence the Sr distribution, generally leading to lower Sr values. The aim of this discussion is not to deny the importance of continental waters on diagenesis of carbonate sediments, only to draw attention towards a possibility of diagenetic consolidation in a marine environment. In fact one has to acknowledge that in such a "closed" system the distinctive grouping into two (four) groups might have been achieved even if the interfering solutions were of a continental type providing other variables remained comparable to those discussed above. The Sr concentrations of rocks from any one environment of deposition may also be influenced by organic activity during diagenesis, by different composition of participating organisms, by different permeability of sediments and by other factors which are at present difficult to evaluate.

However, if "closed" system diagenesis is important we should encounter mainly two distinctive groups of limestones with Sr means about 200 and 600 ppm (as seen in fig. 52) and possibly two groups of dolomites as will be discussed later.

The postulated original mineralogy (Table 11) agrees with the Sr concentrations in figure 52 except for population 3. The sediments of this population are thought to have been originally aragonitic (cf. also Lovenstam, 1963). Thin-section analysis shows recrystallization and late-diagenetic dolomitization of the rocks, indicating an "open" system model of diagenesis. Such a model could easily account for the loss of Sr.

3.2 DISCUSSION

The populations 12, 21, 22, 23, 24 represent types very similar to population 10 with predominantly algal assemblage of organisms, thus indicating original high-Mg? calcite composition of the skeletons. They were also most probably lithified by high-Mg calcite as discussed previously, and thus the overall composition of the lithified rocks was high-Mg calcite. Populations 13, 14, 18, 19, 20 are dark-grey to black, muddy to fine-grained limestones, indicating an euxinic depositional or diagenetic environment. Although they contain some organisms (mainly crinoid ossicles and some algae), the bulk of the rocks is fine-grained matrix. The origin of population 13 is discussed in detail by Veizer (1970a), and is thought to be of a combined inorganic-bacterial origin, whereas populations 14, 18, 19 and 20 are transitional between 13 and 9 (see Table 11).

Population 15 comprises bedded light-grey marly Neocomian limestones with muddy texture and intercalations of marly shales. This type is comparable with the well-known pelagic Biancone Limestones of the Alps. The limestones are characterised by Calpionella and Nannoconus-Radiolaria microfacies. Their high Sr concentration is comparable with the similar pelagic Oberalm Limestones of Malmian age (Flügel and Wedepohl, 1967). Pelagic foraminifera and coccoliths, generally constitute major proportion of such rocks, and recent species of these organisms are composed mainly of stable low-Mg calcite (Blackmonn and Todd, 1959; Arrhenius, 1963). By analogy, one would expect similar mineralogical composition, at the time of deposition, in older rocks. The Sr content of these rocks would be compatible with a "closed" system model if diagenesis was limited mainly to pressure solution around grain margins.

Alternative, although less likely, explanations for the high Sr content of these facies could be as follows:

(1) The original shell mineralogy of some of the Mesozoic-Tertiary organisms (e.g., Tintinidae) was aragonitic.

(2) Flügel and Wedepohl (1967) and Bausch (1968) observed a positive correlation between Insoluble Residue (I.R.) and Sr in part of their samples. Perhaps the clay fraction acted as a barrier to the Sr enriched solutions, squeezed out from the sediments, thus trapping the Sr.

It is conceivable that the clay protects the originally precipitated phase, regardless of its mineralogical composition. This role of shales or other impermeable layers is supported by the discovery of very unstable aragonitic shells from impermeable host rocks as old as Carboniferous (Stehli, 1956; Hallam and O'Hara, 1962). In general, however, I believe that the model outlined above is mainly responsible for the major fractionation of Sr and the clay content is believed to be only an additional factor.

Population 16 consists of early-diagenetic dolomites and 17, late-diagenetic dolomites. Considering the origin of early-diagenetic dolomites (cf. Friedman and Sanders, 1967; Veizer, 1970a) it is postulated that:

(1) They are generally sediments associated with evaporitic "hypersaline", very often lagoonal, sequences;

(2) They are most probably syndiagenetic replacements of original inorganic or biochemical aragonite muds with $\sim$9000 ppm of Sr (cf. Kinsman, 1969);

(3) The basinal and interstitial waters of such regions are generally enriched with respect to ions such as Mg and Sr;

(4) They are usually very fine-grained with high I.R. content and low permeability.

Due to the very high original Sr content, high Sr content of the waters causing the early-diagenetic replacement of the aragonite, and the low

permeability, the final Sr concentrations should remain high, possibly of the order of k x 100 ppm. On the basis of partition coefficient of Sr between aragonite and dolomite determined experimentally by Usdowski (1970) one would expect early diagenetic dolomites to contain greater than about 100 ppm of Sr.

In the case of the late-diagenetic dolomites, one may postulate that:

(1) They are mostly late-diagenetic replacements of original organogenic or organodetrital limestones, which were more or less lithified prior to dolomitization. They might be either of original calcitic (Sr ~1000 ppm) or aragonitic mineralogy (Sr ~ 2000-7000 ppm) or mixtures of the two. However, the unstable aragonite is most probably converted to calcite prior to dolomitization with subsequent loss of Sr from carbonate into pore solutions.

(2) Permeability of such rocks is high and may even increase during dolomitization by 12.1% (Friedman and Sanders, 1967), if one accepts the atom for atom replacement phenomena. Thus the lower initial Sr content and the high permeability should produce a rock with a somewhat lower Sr content, possibly of the order of k x 10 ppm.

Such a bimodal distribution of Sr in dolomites was observed by Stout (1941) and this was attributed to the presence or absence of celestite (Odum, 1950, in Graf, 1960). Although no celestite was detected in the W. Carpathian samples, this explanation may be valid at least for some of the rocks. The association of celestite with "hypersaline" sequences and thus with early diagenetic dolomites could be expected (see p. 97). The higher Sr content of early diagenetic dolomites compared to late diagenetic ones was observed by Awasthi (1970) in the Kroll Belt rocks (Permian or Triassic, Lower Himalaya).

The populations in figure 52 are indeed grouped as predicted in the previous discussion. An additional 1000 unpublished analyses from other

carbonate rocks of the W. Carpathians are consistent with this pattern. Also the data of Kübler (1962), from young and weakly lithified sequences, indicate a higher Sr content in black (euxinic) carbonate muds than in light-coloured organodetrital limestones.

The grouping of the populations into two distinct groups of limestones and possibly two groups of dolomites despite the range of sedimentary environments and original permeabilities, indicates to the author that Sr content is controlled by original mineralogy and the type of diagenesis, rather than by permeability alone.

3.3 COMMENTS

If these conclusions are confirmed by further studies, the Sr content could be a useful addition to the petrographic classification of sedimentary carbonate rocks, and for carbonate muds may even have some advantages over the latter. It should also assist in interpretations of the original mineralogy and genesis of some dolomites and limestones.

The association of limestones + dolomites represented by the "aragonitic" regression is typical mainly of "hypersaline" sequences, whereas the one represented by the "calcitic" regression represents mainly normal marine organogenic and organodetrital sediments (reef, banks, accumulations of organic debris). From the practical point of view, in oil basins which are associated with carbonate sequences, the first group would represent mainly cap-rocks, and the second one mainly reservoir-rocks.

The degree of diagenesis is probably an important factor controlling Sr abundances, and would vary from region to region. In my view, rocks younger than 100 m.y. could contain metastable phases with varying Sr content, whereas rocks older than 800-1000 m.y., even on shield areas, are too strongly influenced by diagenesis (loss of Sr), for the Sr abundance to be

useful in classification and interpretation.

The author recommends extreme caution in assessing the data obtained by this method. The data should be considered as probable only if corroborated by other methods. Because the scatter of Sr within single populations is quite high, the method requires assessment of means and not of single analysis.

Appendix 4

CALCULATIONS OF STRONTIUM ISOTOPIC MODELS

Calculations of the models based on instantaneous fractionation of the crust and upper mantle are simple calculations utilized in everyday practice (cf. for example Hamilton, 1965, p. 113).

Calculations of the continuous transport models were carried out by Dr W. Compston according to the formulae published by Hart and Brooks (1970).

Calculations of the "infinite multistage" fractionation models were based on the Rb and Sr estimates of Armstrong (1968) and calculated in step by step sequence. The procedure is explained in the following description (fig. 53).

The estimates utilized in the present calculations are summarized in Table 13.

Table 13. Estimates of Rb and Sr concentrations in the crust and upper mantle (Armstrong, 1968)

	volume $x10^6 km^3$	total Rb $x\ 10^{20} g$	total Sr $x\ 10^{20} g$	Rb/Sr
crust (= C)	7300	10.875	75.19	0.144
upper mantle (= M)		2.918	282.03	0.010
crust + upper mantle (= C+M)		13.733	357.22	0.039

The unfractionated C+M would contain Rb and Sr concentrations and Rb/Sr ratios as in the third line of Table 13. It is assumed that the C was fractionated in 10 discrete steps with constant rate of fractionation and constant Rb/Sr ratio. Taking the present volume of C as 100%, the required fractionation rate would be 10% of crustal Rb and Sr for each 460 m.y. (10%

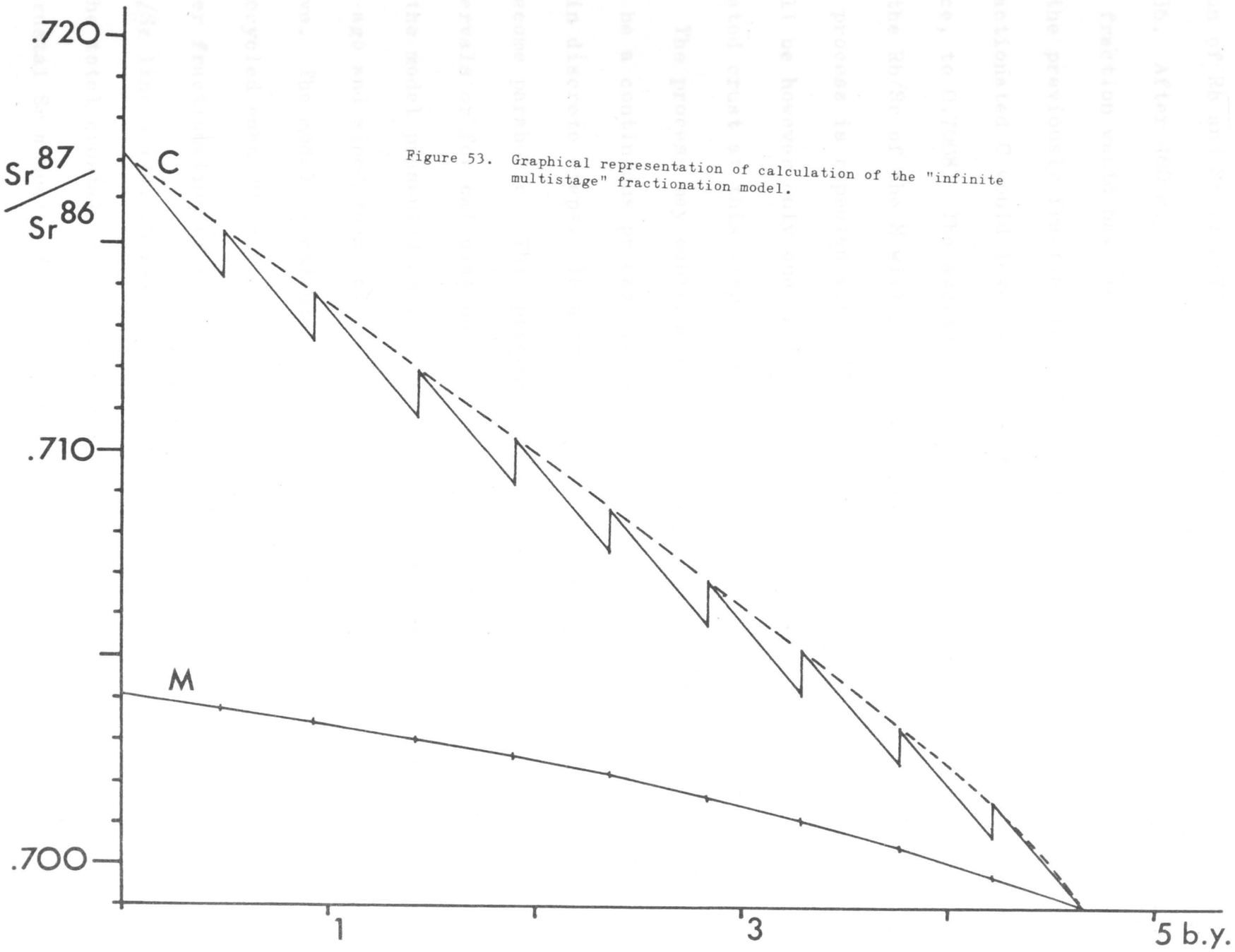


Figure 53. Graphical representation of calculation of the "infinite multistage" fractionation model.

of time). After fractionation of this portion, Sr^{87}/Sr^{86} of C would evolve along Rb/Sr line 0.144 and the M depleted by the fractionated proportion of Rb and Sr (1.0875×10^{20} and 7.519×10^{20} g) along the Rb/Sr line 0.036. After 460 m.y. another 10% of total C was fractionated from M. This fraction would have the Sr^{87}/Sr^{86} of the contemporaneous M (0.6998), whereas the previously fractionated 10% of C evolved to 0.7017. Thus the newly fractionated C would lower the average Sr^{87}/Sr^{86} of C by half of the difference, to 0.7008. The average C again would follow Rb/Sr slope 0.144, whereas the Rb/Sr of the M will be depleted to 0.034. After another 460 m.y. the process is repeated with all consequences. The drop in Sr^{87}/Sr^{86} for C will be however only one third of the C-M difference, since the newly fractionated crust at this stage forms only one third of the contemporaneous total C. The process may continue until present. In nature fractionation of C may be a continuous process (by about 1.6 km^3 $year^{-1}$) and would not proceed in discrete steps. Thus the Sr^{87}/Sr^{86} evolutionary curves of C and M will become parabolic. This procedure may be utilized also for shorter time intervals or for calculation of varying rates of fractionation.

In the model presented in fig. 48 it was assumed that all C was created 3.0 b.y. ago and since then only a process of Sr exchange between C and M was active. The model is calculated on assumption that 12% of total crustal Sr was recycled each 300 m.y. (recycling of approximately 3 km^3 $year^{-1}$).

After fractionation of the total C 3.0 b.y. ago C started to evolve along Rb/Sr line 0.144, whereas M followed the line 0.010. After 300 m.y. 12% of the total crustal Sr was exchanged with the upper mantle Sr. The 12% of crustal Sr amounts of 9.0228×10^{20} g. This amount however represents only 3.22% of Sr in M. So at the time of this exchange Sr^{87}/Sr^{86} of C will decrease by 12% and Sr^{87}/Sr^{86} of M increase by 3.22% of the difference between the contemporaneous ratios of C and M. This calculation may be

repeated until present. Since the process would be continuous rather than discrete, the resulting curves are of parabolic shape.

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